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Exhaust Gas Oxygenate Content

Contract No. CAPE 11-68 (1-69)
Annual Report April 1971

p. 19 - ₱2 - lines 5 and 6

delete "... and total aldehyde concentrations"

p. 19 - ₱2 - lines 7 through 9

delete "The total aldehyde concentration under this method can only be reported as ppm of formaldehyde and are incompatible with the total aldehyde as measured by the AUTOSPECT."

Report No. SRIC 71-6

IMPROVED INSTRUMENTATION FOR DETERMINATION OF EXHAUST GAS OXYGENATE CONTENT

Contract No. CAPE 11-68 (1-69)

Annual Report April 1971

Alan G. Day, III, David P. Beggs,

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With contributions from

Gordon J. Fergusson, F.W. Lampe, Austin Wahrhaftig, Wm. F. Biller, Edward Kraftel, Donald McCubbin, and Donald Kennedy

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ABSTRACT

The application of chemical ionization mass spectrometry to the instrumental analysis of oxygenates in automobile exhaust gases is described. Initial monitoring experiments demonstrated the capability of this technique to simultaneously measure the instantaneous concentration of formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, butyraldehyde, valeraldehyde, and benzaldehyde, and the total aldehyde concentrations.

Preliminary field evaluation established the accuracy and reliability of the instrument via suitable reference tests. The unique ability of this instrument to simultaneously follow the rapidly changing concentrations of nine oxygenates was also verified.

However, it was concluded that the presence of significant amounts of hydrocarbons in the exhaust gas interfered with the measurement of acrolein, crotonaldehyde, benzaldehyde, and tolualdehyde. Further, research resulted in the utilization of ammonia as a reagent gas to overcome this problem and selectively

ionize the unsaturated aldehydes in the presence of the hydrocarbons.

An improved calibration procedure and inlet system were developed. These advancements resulted in a reduction of sample losses in the inlet system and an increase in the accuracy of the instrument. The response time of the total system was lowered to less than one second. The incorporation of these improvements into the system along with the use of ammonia as an alternate reagent gas has eliminated most of the major problems of the instrument.

INTRODUCTION

This is the final report for Phase II of the CAPE-11-68 (1-69) CPA-70-73 contract on the application of chemical ionization to the measurement of oxygenates in automobile exhaust. The high point of this year's work has been the successful field test of AUTOSPECT at Scott Research Labs, Plumsteadville, Pennsylvania. These tests demonstrated the ease with which this instrument can continuously monitor eight different oxygenates simultaneously from the exhaust of a motor vehicle being run on a variable - load dynamometer. From the evaluations of these tests, improvements in inlet design, calibration technique, and the chemical ionization process have been initiated with emphasis in improving the sensitivity to the parts per billion range and eliminating exhaust hydrocarbon interferences and aldehyde memory effects.

Previously, during Phase I of this contract, a prototype mass spectrometer, AUTOSPECT, was designed and built, which combined the chemical ionization technique developed by Field and co-workers

with a direct reading mass spectrograph developed at Scientific Research Instruments.[1] The ionization section of this prototype instrument included a specifically designed ion gun assembly which enabled the production of ions under conditions for chemical ionization i.e., pressure of from 1 to 10 Torr . The analyzer section of the instrument employed the double focusing principle of Mattauch and Herzog and included an array of fixed collectors at integral masses from atomic mass unit 1 to 128.

AUTOSPECT was then used with methane as a reagent gas to successfully produce protonated parent compounds (M + 1) of all oxygenate compounds found in automobile exhaust as identified by Oberdorfer.[2] With the exception of acrolein, crotonaldehyde, benzaldehyde, and tolualdehyde, no interferences were found to be present with the aldehydes and ketones due to the presence of hydrocarbons when measured with methane as the reagent gas.

After the preliminary field testing of AUTOSPECT during Phase II it was found that with a vehicle with a 1969 style PVC valve pollution device, enough hydrocarbons were emitted as to significantly interfere with above mentioned aldehydes to merit

an investigation of other compounds as reagent gases. Ammonia was found to selectively ionize acrolein, crotonaldehyde, benzaldehyde, and tolualdehyde to produce the parent compound. This is discussed in more detail in a later section of this report.

Phase II also included the successful development of a calibration procedure whereby a liquid sample of an aldehyde or ketone was injected into a flowing stream of nitrogen gas at a fixed rate. The preliminary field tests pointed out a need for improvement in this area. It was found that under field conditions this system was too time consuming and too sensitive to temperature fluctuations.

Also during preliminary investigations it was discovered that great care must be taken in the design of the exhaust sample line, particulate filter and sample-reagent mixing chamber so as to prevent deposition of polymerized formaldehyde. This is discussed in more detail in a later section.

PRELIMINARY LABORATORY EXPERIMENTS

Response Time Measurements

Preliminary measurements of the response time of the total system were made. The results of these experiments indicated that the response time constant which was applicable to raw exhaust gas monitoring was three seconds. Since the response time of the analysis system has been previously determined to be less than one microsecond, the response time of the total system is a reflection of the response time constant of the heated sample inlet system itself.

Typical results of measurements of the response time of the fixed collector direct reading mass spectrometer system coupled to the heated inlet are shown in Figures 1 and 2. These plots show the response of the instrument to the injections of formaldehyde and benzaldehyde, respectively. These measurements were performed by injecting a step pulse of the selected aldehyde at approximately 0.01 milliliters per minute into a stream of nitrogen gas flowing at 10 liters per minute. These

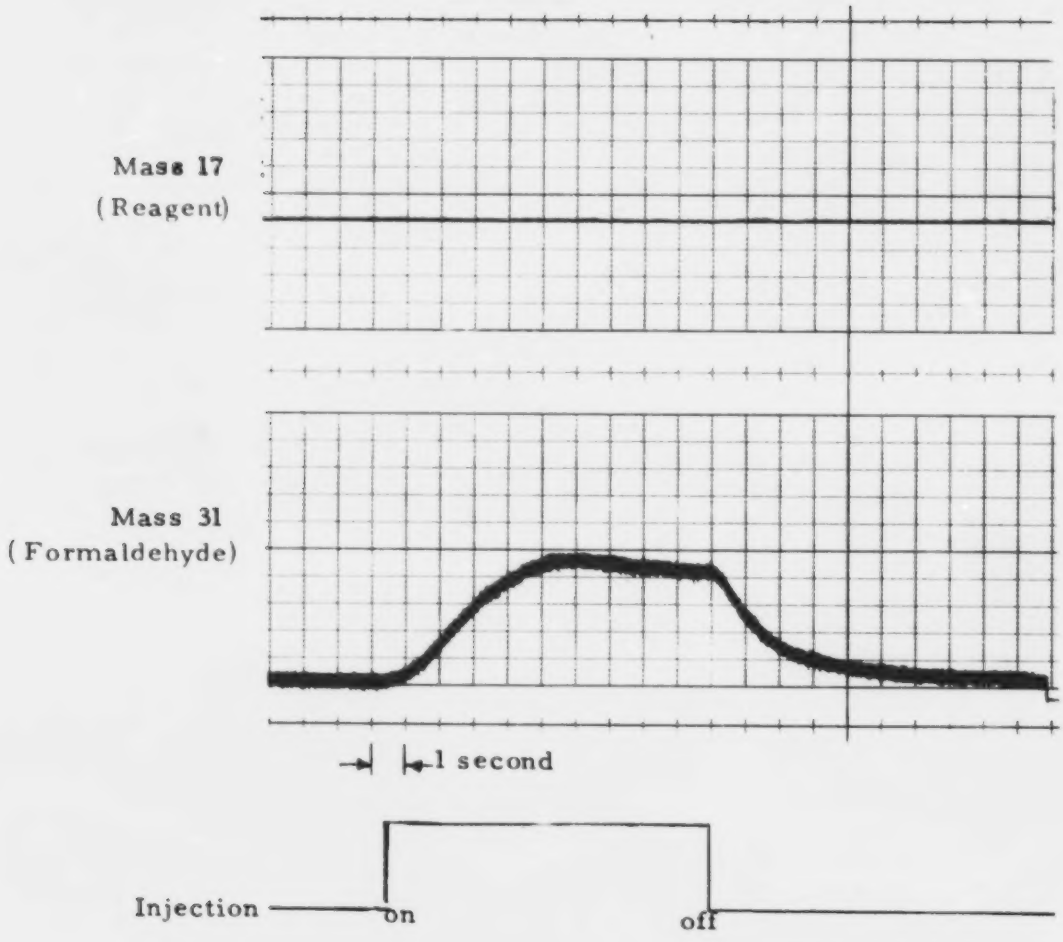

Figure 1 Response of Chemical Ionization Direct Reading Mass Spectrometer to a Step Injection of Formaldehyde at the 10 ppm level

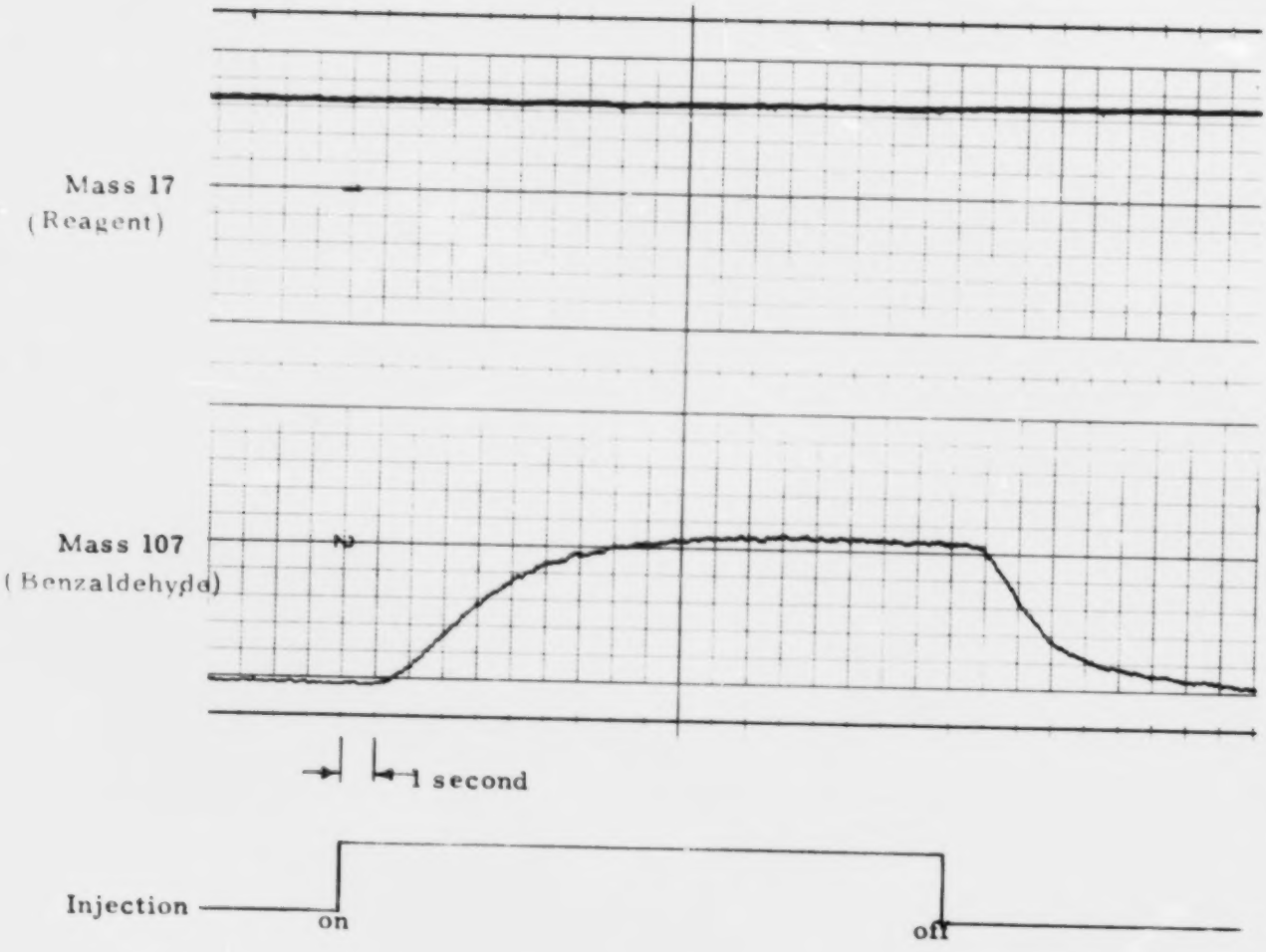

Figure 2 Response of Chemical Ionization Direct Reading Mass Spectrometer to a Step Injection of Benzaldehyde at the 10 ppm level

plots of the results show the effects of the step injections upon the channels representing formaldehyde and benzaldehyde in the mass spectrometer system. The effect of these step injections upon the reagent ions (mass 17) is shown to be negligible. This demonstrates that there are no spurious effects due to the loss of an inordinate amount of reagent ions.

These results correspond to an experimental time constant of approximately three seconds for both aldehydes. This same time constant was observed for all other aldehydes measured. The time constant of the inlet system was reduced to one second by improving the total inlet system package. This improved system is covered in a later section.

Investigation of Potential Interferences

The use of methane as a reagent gas in chemical ionization provides distinct and accurate measurement for all but a few of the aldehydes and ketones present in automobile exhaust gases. The saturated aldehydes and ketones are not impaired by interferences from hydrocarbons. The oxygenated compounds give ions principally at the parent mass plus one ion, while the hydrocarbons of the same molecular weight produce ions at the parent mass minus one.

However, hydrocarbons do interfere with unsaturated aldehydes. Acrolein produces an ion at m/e 57 via chemical ionization with methane. Butyl ions also at m/e 57 may be produced by proton transfer to the butenes or by hydride ion transfer to the butanes. Thus the presence of butenes or butanes in automobile exhaust will interfere with the measurement of acrolein when methane is used as a reagent gas. Pentenes and pentanes interfere in the measurement of crotonaldehyde via a similar mechanism. The presence of pentenes, pentanes and crotonaldehyde will all produce an ion at m/e 71 via chemical ionization with methane as the reagent gas. One

of the advantages of chemical ionization is that one can vary the reagent gas and thus vary the amount of energy which is transferred to the molecule upon ionization. Since the hydrocarbons have a different proton affinity than the unsaturated aldehydes, it should be possible to find a reagent gas which will ionize hydrocarbons and not ionize the unsaturated aldehydes via the chemical ionization process.

Because of its omnipresence, water was utilized as a reagent gas in an attempt to modify or eliminate the interference of hydrocarbons in the measurement of unsaturated aldehydes. The typical spectra of water at 1 Torr is shown in Figure 3. The various ions in the spectra are produced by a series of equilibrium reactions. These equilibria along with the precursor reactions are shown below.

$$H_2O + e^- \longrightarrow H_2O^+ + 2e^-$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$$

$$H_3O^+ + H_2O \rightleftharpoons H(H_2O)_2^+$$

$$H(H_2O)_n^+ + H_2O \rightleftharpoons H(H_2O)_{n+1}^+$$

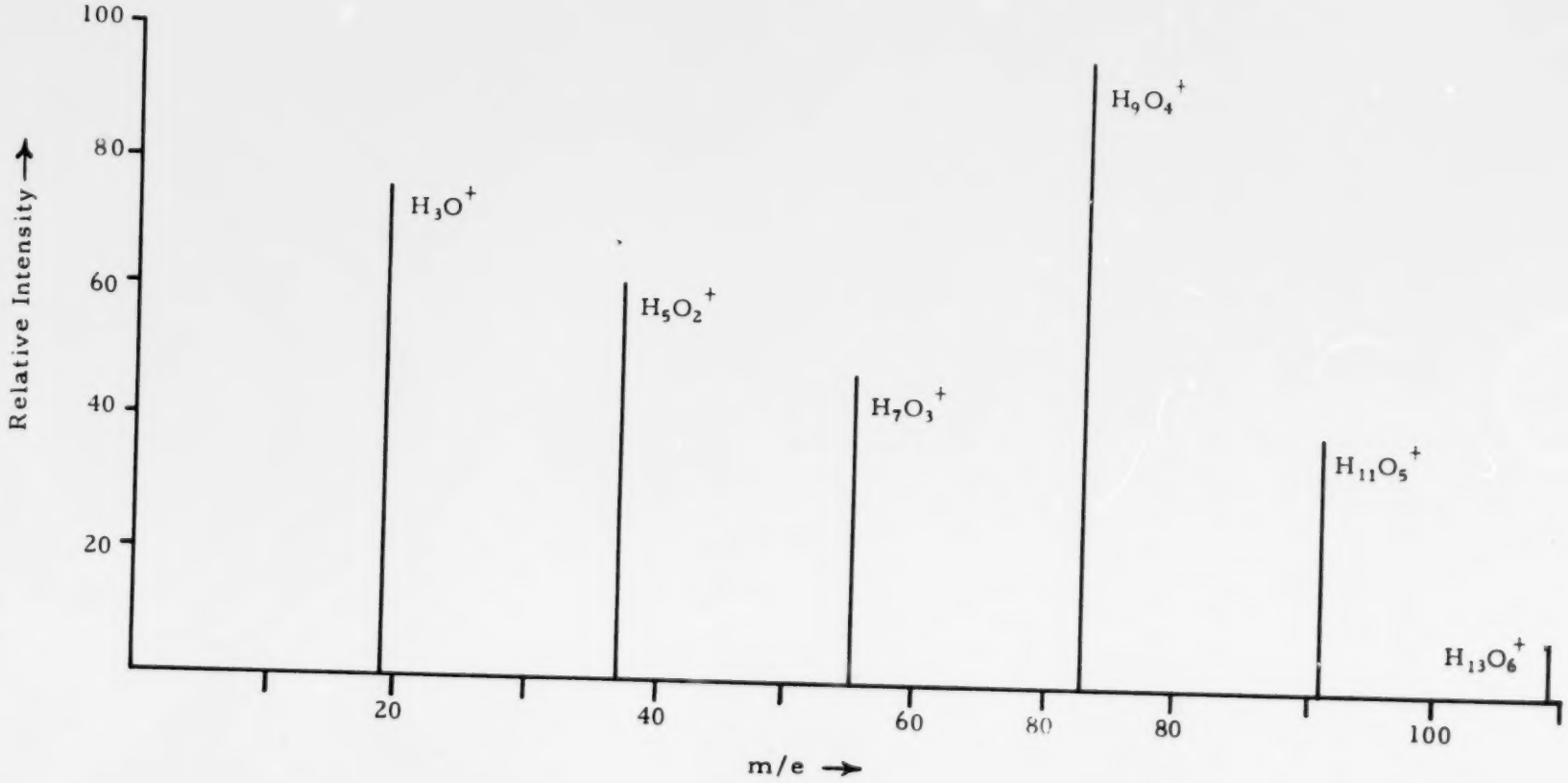

Figure 3. High Pressure Spectrum of Water

The initial H_3O^+ ion is produced by a proton transfer reaction from one water molecule to another. The other ions in the equilibrium system are produced by the addition of one or more water molecules to this H_3O^+ ion. In several experiments it was found that water will indeed proton transfer to the various aldehydes in automobile exhaust. However, water will also react with the hydrocarbons and thus produce the same interferences at the m/e values of 57 and 71 as were experienced with methane as the reagent gas. It was therefore concluded that water would not be a suitable substitute as a reagent gas in an effort to eliminate hydrocarbon interferences. It was later discovered that ammonia may be used as a reagent gas to distinguish between the unsaturated aldehydes and their interfering hydrocarbon compounds. This approach is discussed in detail in a later section.

Particular interference in the measurement of aldehydes by the presence of H_2, N_2, O_2, H_2O, CO, CO_2, NOx, H_2S and SO_2 was determined to be negligible. Experiments were undertaken to verify that the quantitative measurement of each of the aldehydes involved in this study were not in error due to the presence of the above constituents of automobile exhaust.

Automobile Exhaust Monitoring

The initial tests using the direct reading chemical ionization mass spectrometer to monitor raw exhaust gases were conducted at the SRIC laboratory in Baltimore, Maryland. These measurements were accomplished using the heated inlet system and continuous monitoring of the fixed collectors. The aldehydes monitored included formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, butyraldehyde, valeraldehyde, benzaldehyde, and the total aldehyde concentrations. Calibration of the system for each of these aldehydes was accomplished by injecting the aldehydes at a known rate into a stream of nitrogen gas simulating the automobile exhaust. These calibrations were carried out in the concentration range from 1-100 parts per million and the response was linear to within 10 percent over this concentration range. An example of a calibration response is shown in Figure 4.

Some of the results of the initial exhaust tests are shown in Figures 5 and 6. During the calibration measurements the system was operated using calibrated injections of pure individual

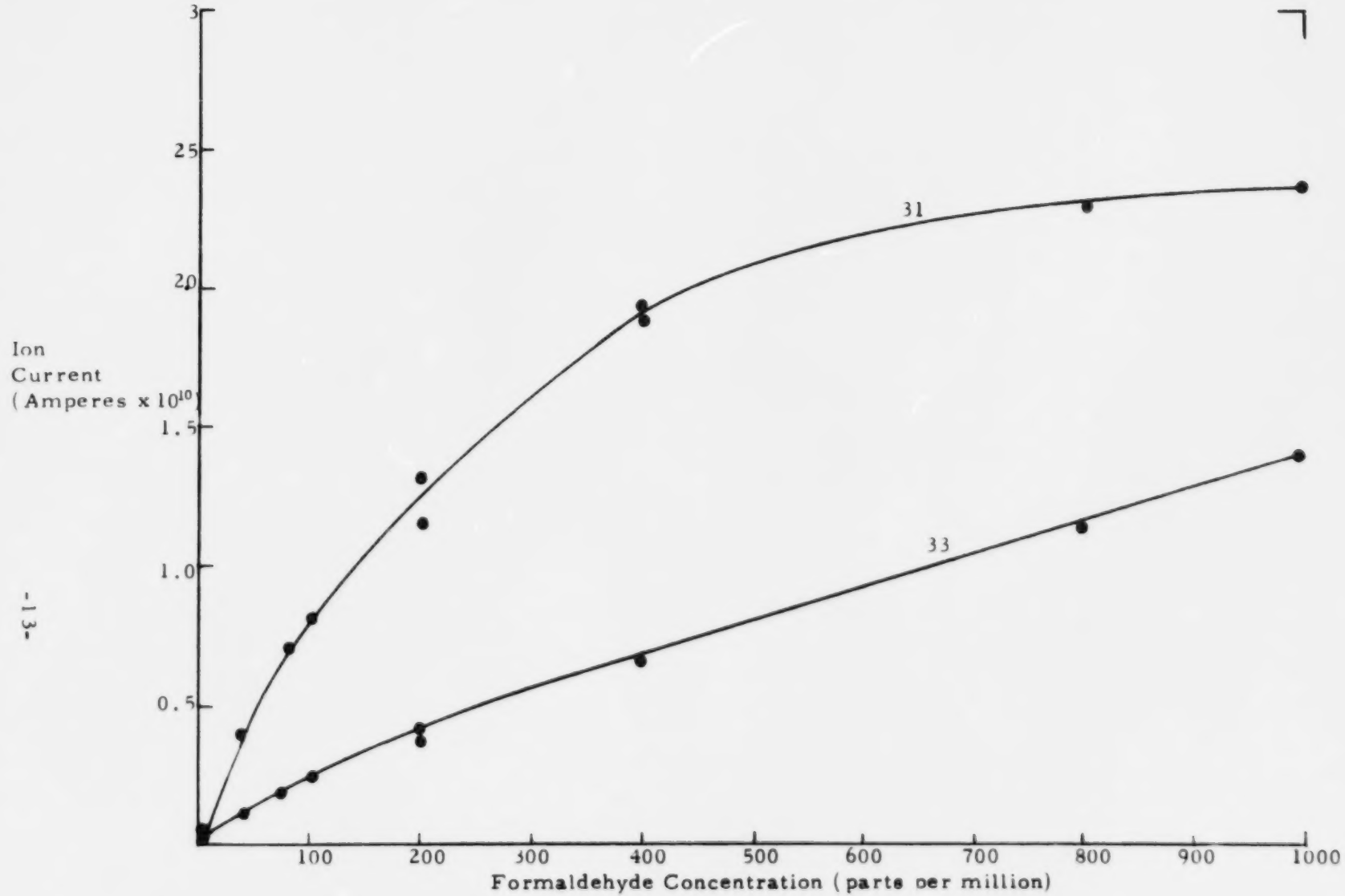

Figure 4 - Response of the direct reading chemical ionization mass spectrometer at masses 31 and 33 as a function of formaldehyde concentration in nitrogen using methane as the reagent gas at 1 part to 2 parts nitrogen. The formaldehyde was injected as formalin solution containing 38% formaldehyde and 13% methanol in water. The response at mass 33 is due to the protonated methanol.

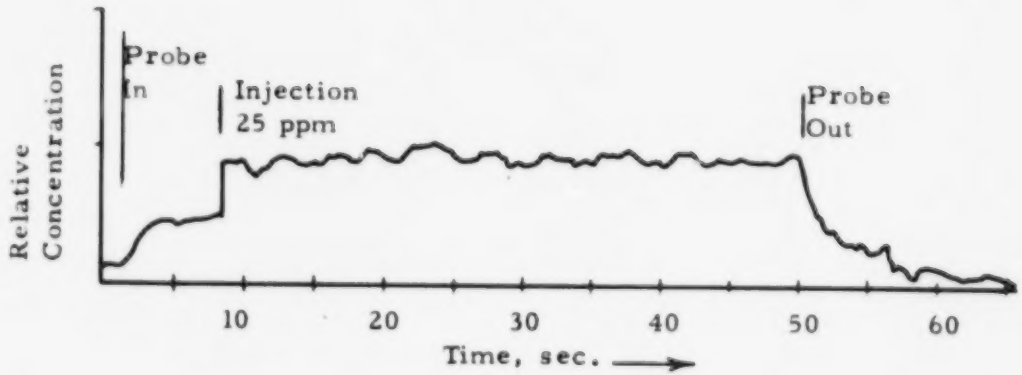

Figure 5 Monitor of Acrolein Concentration During Injection of 25 ppm Acrolein

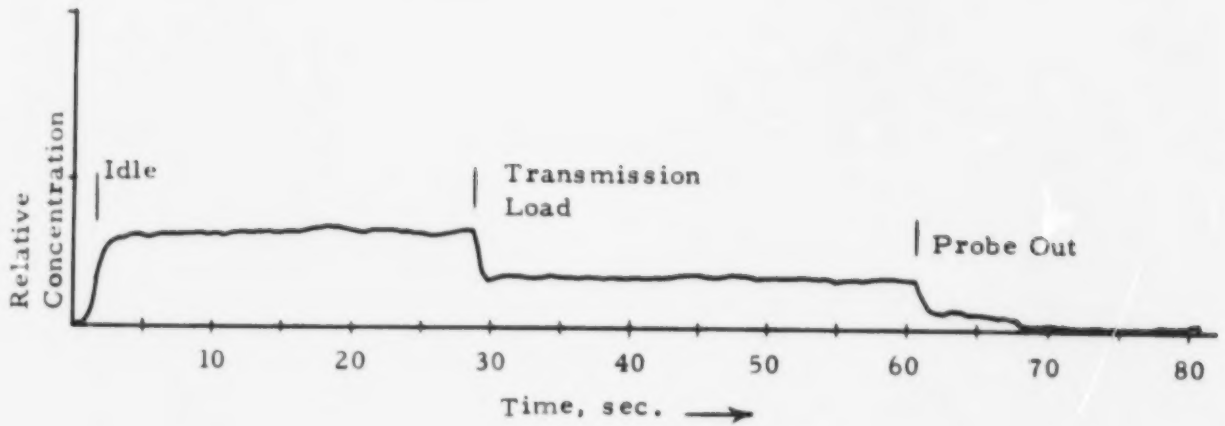

Figure 6 Monitor of Formaldehyde Concentration

aldehydes in nitrogen as well as using mixtures of the aldehydes. No significant synergistic effects involving the mixtures of the various aldehydes were observed.

The operation of the direct reading chemical ionization mass spectrometer system was demonstrated to the APRAC Project Group, Cape 11-68, on July 28, 1970. The response of the system to individual aldehydes was demonstrated as well as continuous measurements on raw engine exhaust. The system was operated measuring the aldehydes emitted by a 1969 Cutlass as well as an older car.

PRELIMINARY FIELD EVALUATION

Introduction

Initial exhaust monitoring studies were undertaken at the laboratories of Scientific Research Instruments Corporation in Baltimore, Maryland. The results of these experiments demonstrated the ease and speed of measurement using this method. However, further studies were warranted to determine the accuracy and overall reliability of the instrument under varying conditions.

Observation of changes in the most useful parameters could be obtained by accelerating, decelerating, and maintaining the speed of an automobile under proper load conditions. These tests could not be easily accomplished at the laboratories of Scientific Research Instruments Corporation. At this point, negotiations were completed to provide the use of the automobile dynamometer facilities at Scott Research Laboratories, Inc. in Plumsteadville, Pennsylvania.

During the month of October 1970, a preliminary field evaluation of the Scientific Research Instruments Corporation

oxygenate analyzer program was conducted at Scott Research Laboratories, Inc., with the cooperation of Dr. William Biller. This program included a series of steady state experiments measuring selected oxygenate output of a 1969 Chevrolet pick-up truck run on a dynamometer at constant speeds of zero, thirty, and fifty miles per hour. Also oxygenate levels were measured as the Chevrolet truck was run through a series of seven mode California Standard Cycles.

In an effort to determine the accuracy and reproducibility of the Scientific Research Instruments Corporation instrument, duplicate reference samples were collected under the direction of Dr. Emmett Jacobs of E.I. DuPont deNemours and Company. These samples, collected during the steady state experiments, were subsequently analyzed by the DNPH method and compared with the results obtained by the Scientific Research Instruments Corporation AUTOSPECT.

Results

A series of steady state experiments measuring selected oxygenate outputs of a 1969 Chevrolet truck on a dynamometer were accomplished. Reference tests, using the DNPH method, were conducted under the direction of Dr. Emmett Jacobs of DuPont. A comparison of the results of these two methods of analyses are shown in Table I. These results, in general, show some agreement. The discrepancies are discussed in the next section.

Another series of measurements for steady state runs of zero, thirty, and fifty miles per hour were made in conjunction with those of Scott Research Laboratories to be analyzed using the chromatropic acid method. This latter method can only be used to determine formaldehyde and total aldehyde concentrations. The formaldehyde results are given in Table II. The total aldehyde concentration under this method can only be reported as ppm of formaldehyde and are incompatible with the total aldehyde as measured by the AUTOSPECT. The results are in agreement and show satisfactory reproducibility.

TABLE I - AUTOSPECT MEASUREMENTS VS. DUPONT ANALYSES, TEST CONDUCTED AT SCOTT LABORATORIES, Inc. (Preliminary Dynamometer Series - 1969 Chevrolet Truck, All Concentrations in Parts Per Million)

OXYGENATE	HOT-IDLE		30 MPH		50MPH	
	Autospect	DuPont	Autospect	DuPont	Autospect	DuPont
Formaldehyde	4.1	7.9	42	60	44	59
Acetaldehyde	1.4	1.0	8.4	7.3	6.0	7.3
Acrolein	4.2	0.2	8.8	2.8	5.5	1.9
Propionaldehyde	0.3	0.2	2.1	1.4	1.6	1.4
Crotonaldehyde	2.0	1.3	5.4	4.6	4.0	4.3
Butyraldehyde	0.3	0.2	1.2	1.4	0.8	1.8
Benzaldehyde	2.6	0.8	3.8	3.4	2.6	3.4
Tolualdehyde	1.4	0.2	2.1	0.9	0.8	0.8
Total Aldehyde	16	12	74	82	65	80

TABLE II - AUTOSPECT MEASUREMENTS VS. S.R.L. CHROMOTROPIC ACID ANALYSES

MODE	FORMALDEHYDE (p.p.m.)	
	Autospect	Chromotropic Acid
Cold-Idle	6	9
30 m.p.h.	48	39
50 m.p.h.	50	53
Hot-Idle	5	8
30 m.p.h.	36	38
50 m.p.h.	46	40

In order to establish the capability of AUTOSPECT to accurately measure the concentrations of many oxygenates which are rapidly changing, dynamic experiments were conducted. A suitable test of these dynamic aspects as well as the response time is the seven mode California Standard Cycle. A graphical depiction of this cycle is shown in Figure 7. A series of dynamics runs including the instantaneous measurement of the exhaust of the 1969 Chevy truck run through standard California seven mode cycles on a dynamometer were made and the results are shown in Figures 8 - 10. The ability of the AUTOSPECT to follow a continuous varying oxygenate concentration was effectively proven. The response time of the instrument was measured to be less than one second. The traces of acrolein, crotonaldehyde, benzaldehyde, and tolualdehyde resemble the traces of the total hydrocarbon concentration thus confirming the effect of large hydrocarbon concentrations at their mass numbers. Otherwise, the traces of formaldehyde, acetaldehyde, and propionaldehyde appear to be representative of the true concentrations of these oxygenates during this cycle.

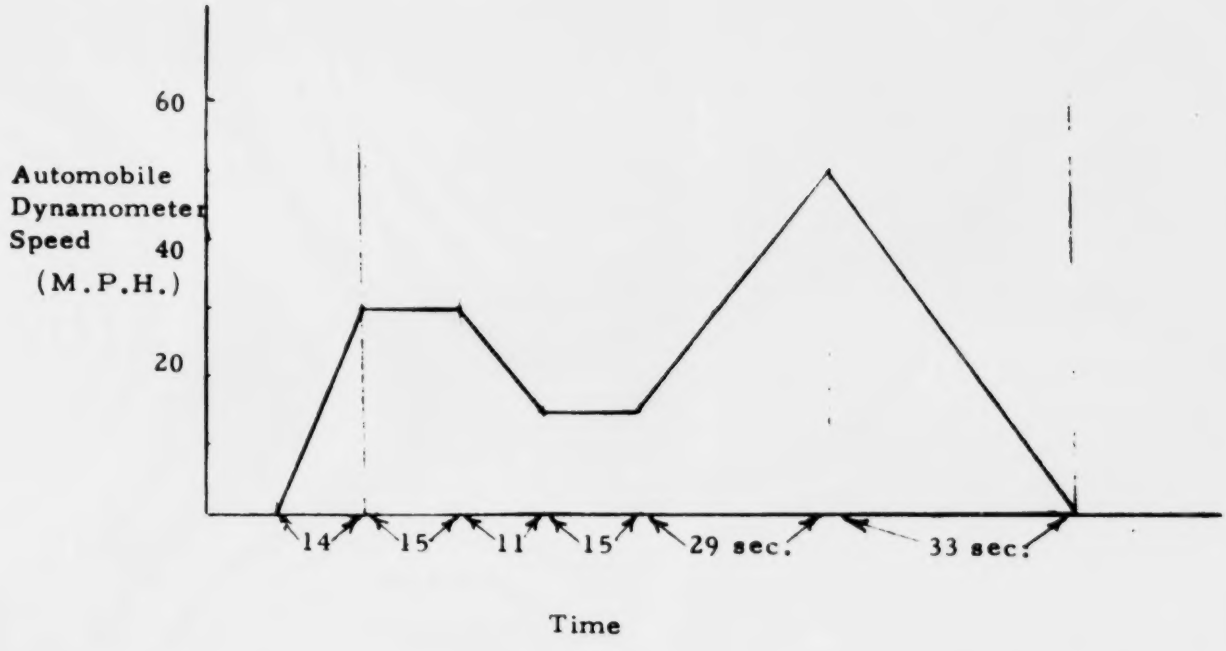

Figure 7 - Graphical Depiction of the 7 Mode California Standard Cycle

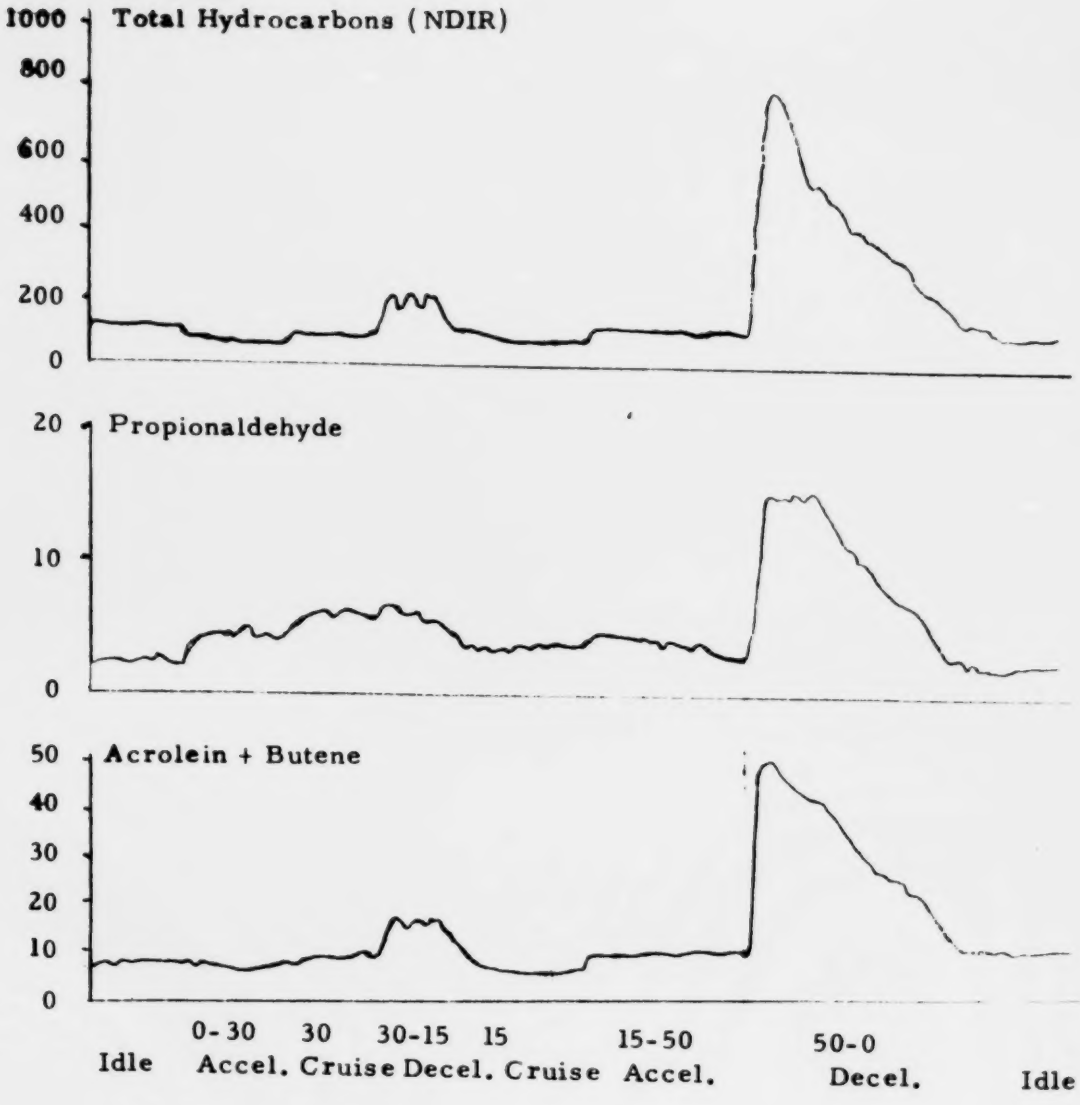

Figure 8 - (Run 1)
Concentrations of Selected Components of Exhaust Gas Measured During a 7 Mode California Cycle Run on a Dynamometer.

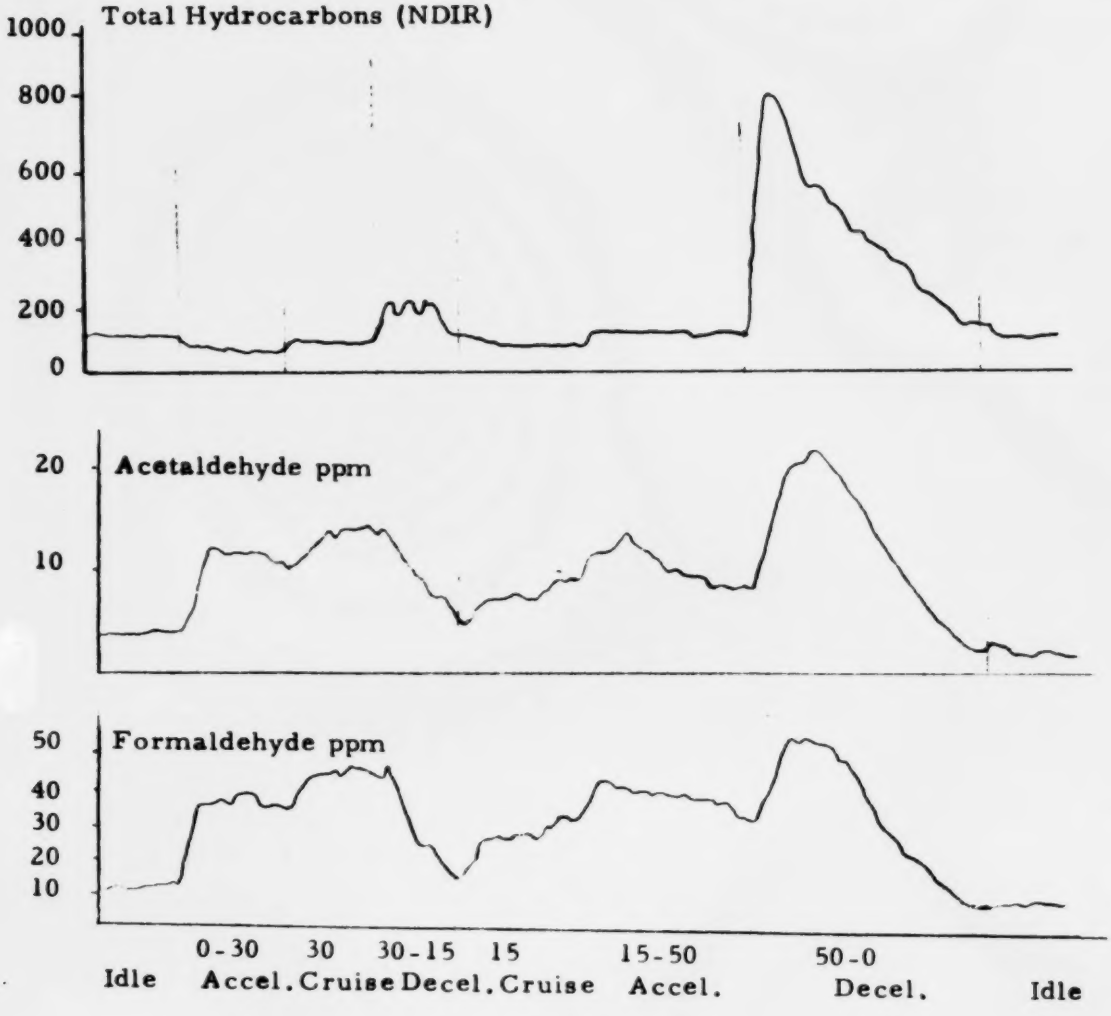

Figure 9 - (Run 1)
Concentrations of Selected Components of Exhaust Gas Measured During a 7 Mode California Cycle Run on a Dynamometer.

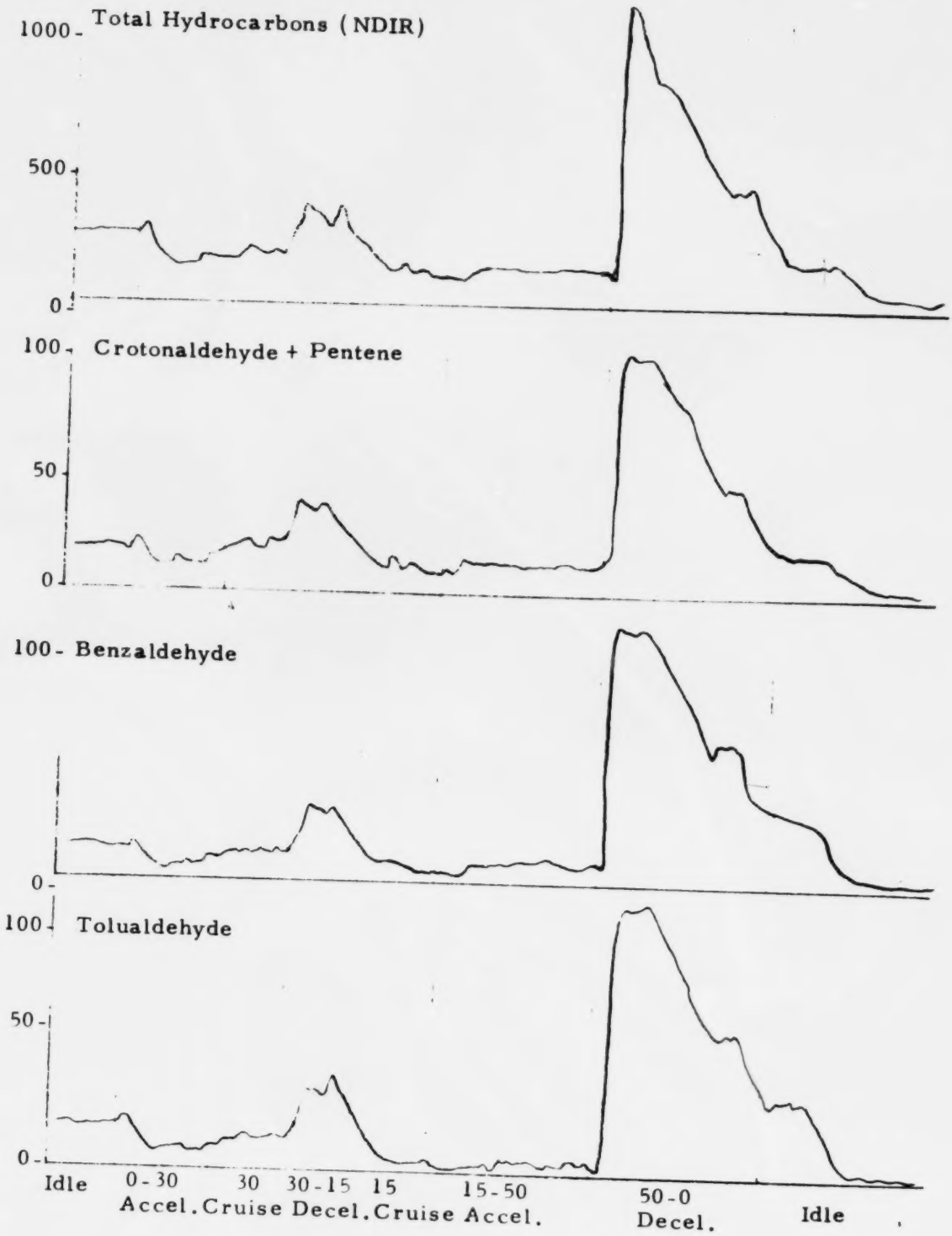

Figure 10 - (Run 2)
Concentrations of Selected Components of Exhaust Gas Measured During a 7 Mode California Cycle Run on a Dynamometer.

Since automobile exhaust contains about five percent water vapor, which is in itself an excellent reagent gas, experiments were performed to determine the feasibility of water as the reagent gas. The use of this technique would enable the elimination of the addition of a reagent gas during measurements. It was found that during the deceleration modes of the dynamic cycle runs on a dynamometer, there was a sufficient drop in water vapor concentration and concurrent rise in the hydrocarbon concentration to cause incomplete ionization of the oxygenates.

The response time of the total instrument and inlet system was determined by rapidly accelerating the automobile and measuring the lag time of the instrument response. The results shown in Figure 11 show the response time to be less than one second.

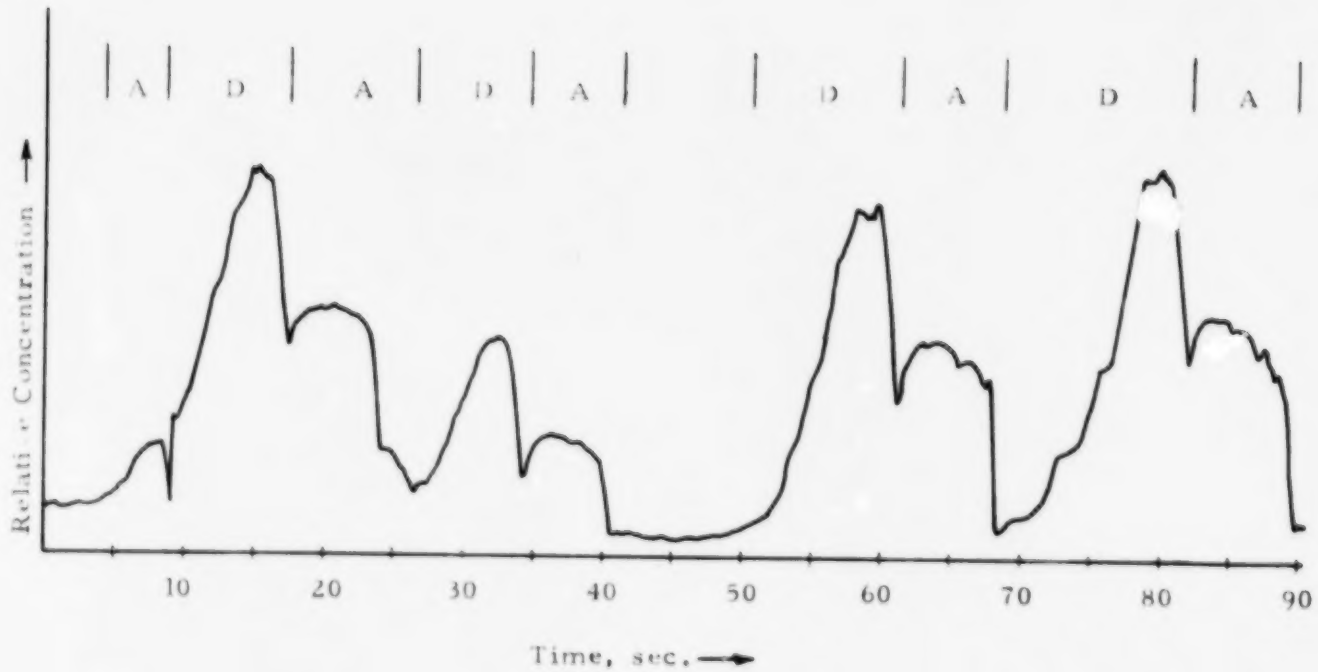

Figure 11 Response Time Measurements of the Total Instrument and Inlet System

A : Acceleration
D : Deceleration

Discussion

The comparison of the results of the steady state measurements in Table I show some agreement and point out a need for further improvements in the AUTOSPECT System. The discrepancies in total aldehydes were due to disagreements in the formaldehyde and acrolein concentrations. It must be pointed out that the measurements obtained from AUTOSPECT were corrected data. The aldehydes were measured before and after scrubbing the exhaust gas stream with a $NaHSO_3$ aqueous solution. This was needed because it was noted during the experiment that residual amounts of aldehydes were remaining in the inlet system. This would account for the discrepancies in the comparison of the results of formaldehyde.

In the Hot-Idle phase, it appears that the presence of hydrocarbons interfere with the measurement of the unsaturated aldehydes. The lack of correlation in the acrolein results at 30 MPH and 50 MPH seems inconsistent with the other data. This may be cause by experimental error or the presence of butenes or butanes in the absence of other hydrocarbons under these conditions.

The accuracy and precision of the chemical ionization mass spectrometric technique has already been well established. Thus, errors of measurement in the AUTOSPECT probably lie

in the inlet system. In collaboration with Scott Research Laboratories, Inc. an improved inlet system has been designed and built. This system includes a better calibration mechanism and an improved sampling technique. This revised inlet system is incorporated into the present instrument and will be used for all further testing. A more detailed discussion of this inlet system is covered in a later section.

The discrepancy in the acrolein measurements is due primarily to the relatively large amounts of butyl ions formed in the mass spectrometer from butene, butane, and higher molecular weight hydrocarbon molecules. To a lesser extent crotonaldehyde, benzaldehyde, and tolualdehyde have interferences due to pentyl, xylyl, and substituted benzyl ions respectively. To minimize these interferences, research has been done using ammonia as a reagent gas. As discussed in another section, it has been found that ammonia selectively ionizes aldehydes without ionizing their hydrocarbon counterparts.

The results shown in Figures 8-10 effectively demonstrate the ability of AUTOSPECT to follow a continously varying oxygenate concentration. The traces of masses 57, acrolein ;

71, crotonaldehyde; 107 benzaldehyde; and 121, tolualdehyde, closely resemble the traces of the total hydrocarbon concentration. This confirms the effect of large hydrocarbon concentrations at these mass numbers. The traces of formaldehyde, acetaldehyde, and propionaldehyde appear to be representative of the true concentrations of these oxygenates during this cycle. Presumably if the hydrocarbon interferences were removed from the measurement of acrolein, crotonaldehyde, benzaldehyde and tolualdehyde, the form of their traces would be more similar to the traces of the other aldehydes shown in Figures 8-9.

Improved calibration and sampling technology will be included in the construction of a modified inlet line which will be used for further testing. Several new reagent gases will be investigated further to determine their effectiveness in eliminating hydrocarbon interferences in the measurement of acrolein, crotonaldehyde, benzaldehyde, and tolualdehyde. These improvements will result in a complete instrument of unique accuracy, precision, and speed of measurement of oxygenates.

The use of water as a reagent gas provided the possibility of the elimination of the reagent gas addition phase of the inlet

system. However, the concentration of water in the exhaust decreases sufficiently during deceleration to cause conditions which would prevent complete ionization of the oxygenates present. This condition is aggravated by the correspondingly large increase of hydrocarbons which absorb much of the ionizing process. This effect was especially prevalent in measurements of an old or improperly tuned engine. It is possible to overcome this problem by supplemental injection of water vapor but it was decided that methane is superior in overall performance as a reagent gas for measurement of oxygenates in automobile exhaust.

IMPROVEMENTS IN TECHNIQUE AND APPARATUS

Calibration System

A new calibration method has been devised as an improvement over the previous constant rate injection system. It was found from field evaluation runs that too much time was wasted by having to carefully inject each aldehyde individually and that instabilities resulted outside the clean conditions of the laboratory. The new calibration procedure involves generating a known gaseous mixture of the aldehydes from diffusion tubes. The theory and practice for this method are reasonably well defined.[3,4]

The rate of diffusion of a liquid at constant temperature out of a diffusion tube of known dimensions is given by the following equation:

$$r = 2.81 \times 10^{6} \frac{DMPA}{TL} \ln \frac{P}{P-p}$$

where r = rate of diffusion of vapor out of diffusion tube, micrograms/second

D = molecular diffusion coefficient of the vapor into the diluent gas, square centimeters/second

M = molecular weight of vapor

P = total pressure in diffusion cell, atmospheres

A = cross sectional area of diffusional tube, square centimeters

p = partial pressure at a temperature T of the vapor, atmospheres

T = temperature ^0K

L = length of diffusional path, centimeters

This rate of diffusion is sensitive to P, the total pressure, and T, temperature, as shown by Altshuller[3]. He has shown that for a total pressure change of 20 Torr there is a change of 1% to 3% as p, the partial pressure of the aldehyde, is increased from 5 Torr to 600 Torr suggesting that the aldehyde diffusion tubes should be operated at a temperature where the p is low. Also he has determined that for a change in temperature of 1^0C there is a change of 4.9% in the diffusion rate for n-hexane suggesting that the system be carefully thermostated. Figure 12 shows the vapor pressure plots versus temperature for most of the aldehydes and hydrocarbons to be used. From this plot and the above equation a change of 2.8 percent in diffusion rate for a 1% change in temperature was calculated for crotonaldehyde at 30^0C.

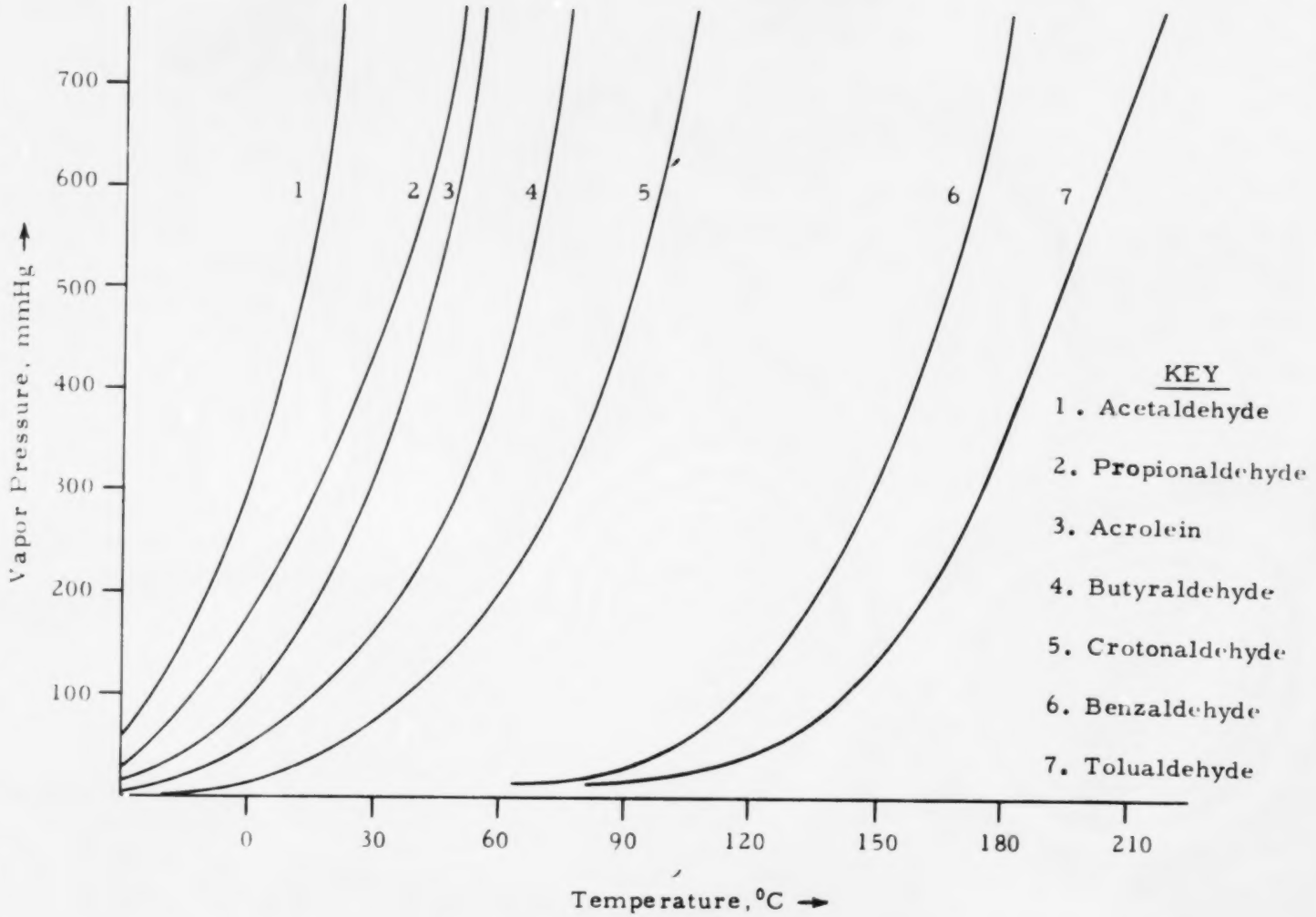

Figure 12. Vapor Pressure of Aldehyde as a Function of Temperature

The proposed calibration system will include a diffusion tube for each aldehyde held at a constant temperature of $\pm$ 0.5°C in a constantly stirred water bath. A diffusion tube for each aldehyde will be connected in tandem with a tube made of Teflon of the α -polymer of formaldehyde via a monitored nitrogen gas flow. A diagram of this system is shown in Figure 13. The amount of time to approach steady state conditions to within $\pm$ 0.5% is given by the equation:

$$t = \frac{L^2}{2D}$$ where t = total time in seconds

For benzaldehyde in a diffusion tube where L = 5 cms., the time to approach equilibrium is calculated to be, t = 3 minutes.

As of yet, no experimental values for D, the diffusion coefficient, of aldehydes have been found, but two methods have been found where the coefficient can be estimated[5,6] to within 5%. One method according to Roberts, is based on

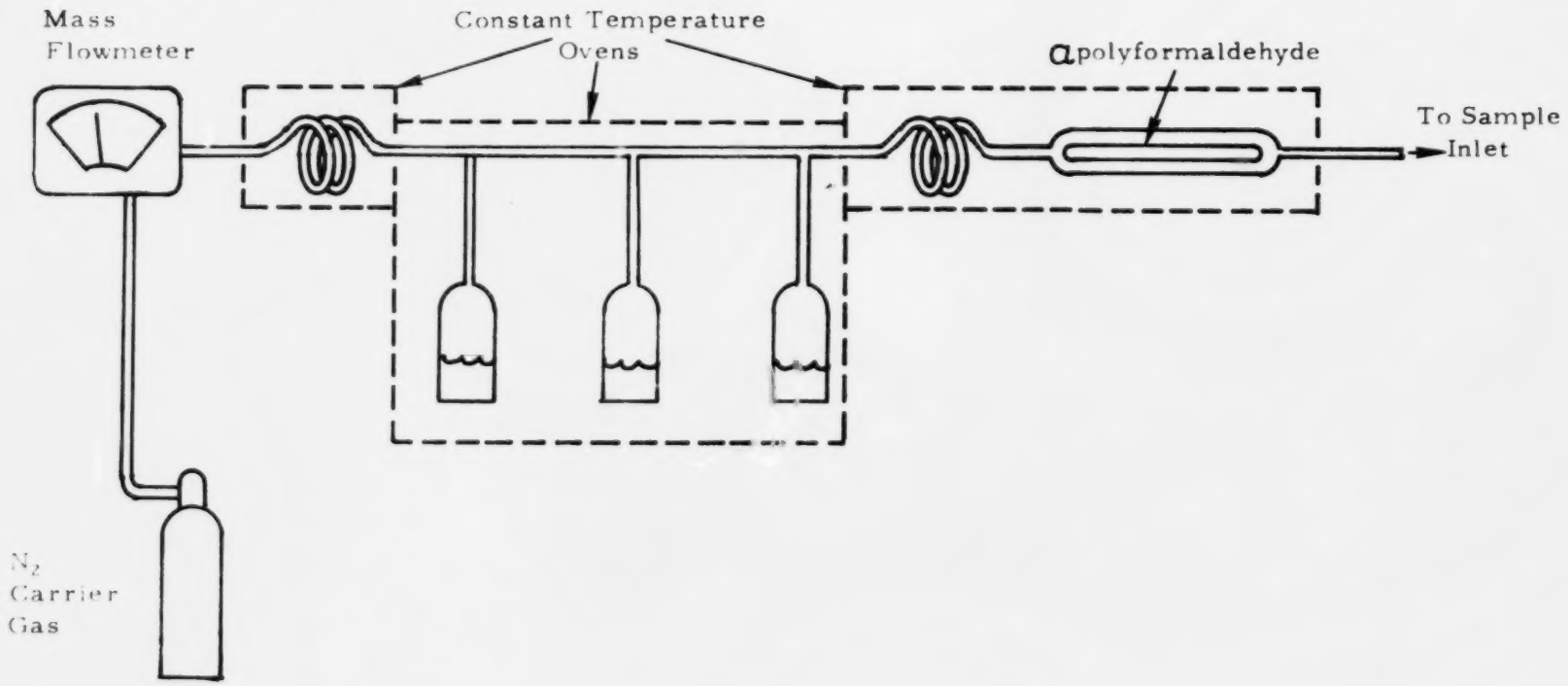

Figure 13 Diagram of Proposed Calibration System for Aldehydes in the PPM Range

predetermined atomic and structual force constants and is calculated from the equation:

$$D = 4.4\left[\left(\frac{E}{K}\right)^{-0.5} d^{-1.5} \left(1 - 0.5\delta^{0.6}\right)^{-1}\right]^{0.75}$$

where

$$\frac{E}{K} = \frac{0.75\,T_b}{0.57 + \sum \Delta_t} \qquad d = \left(\frac{E\,V_c}{1.27}\right)^{0.33} \qquad \delta = \frac{\mu^2}{2E d^3}$$

and

T_b = Normal boiling point, ^0K

Δ_t = Atomic and structual constants

V_c = Atomic and group constants centimeters/gram mole

μ = Dipole moment, 10^{18} ESU centimeters

E = Force constant

K = Boltzmann's Constant

A simpler method, that of Fuller, Schettler and Gliddings, involves knowing values of additive atomic volumes for C, H, and O determined from a least squares fit program into which data from previous diffusion coefficient experiments has been fed. The diffusion coefficient is obtained from this equation:

$$D = \frac{10^{-3}\, T^{1.75} \left(\frac{1}{M_a} + \frac{1}{M_b}\right)^{0.5}}{P\left[\left(\sum_a V_i\right)^{\frac{1}{3}} + \left(\sum_b V_i\right)^{\frac{1}{3}}\right]^2}$$

where

T = temperature ^{o}K

Ma, Mb = molecular weight, grams/mole

P = pressure, atmospheres

$\sum_a V_i, \sum_b V_i$ = empirically determined diffusion volume, atomic volume

The temperature dependency of D is given by the equation:

$$D = Do \left(\frac{T}{273}\right)^3 \frac{760}{P}$$

An example calculation of the diffusion constant of benzaldehyde by the method of Fuller, Schettler and Giddings is given in the Appendix. Table III shows a comparison of the diffusion coefficients determined for aldehydes from both the above methods.

TABLE III: Comparison of Empirically Determined Diffusion Coefficients of Aldehydes and Hydrocarbons (Calculated for 273°K)

Compounds	$^{T}D(1)$ (cm^2/sec)	$^{TT}D(2)$ (cm^2/sec)
Acetaldehyde	*	0.115
Acrolein	0.0975	0.0976
Propionaldehyde	0.1040	0.0946
Crotonaldehyde	0.0894	0.0840
Iso-Butyraldehyde	0.0777	0.0820
Benzaldehyde	0.0599	0.0702
p-Tolualdehyde	*	0.0658
Pentene	*	0.0777
Xylene	0.0541	0.0670

*Adequate information not available

$^{T}D(1)$ Method of Roberts

$^{TT}D(2)$ Method of Fuller, Schettler and Giddings

Later, these empirically determined coefficients will be correlated with concentration values experimentally determined by the DNPH method.

The production of formaldehyde at known gaseous concentrations presents a special problem in that it so readily polymerizes on the walls of the tubing. The injection of a formula in solution at a known rate is still an attractive method in this case if temperatures are carefully maintained. Another attractive method, as suggested by John E. Sigsby, is to use a solid alpha polymer form of formaldehyde sealed in a tube made of Teflon . (In this case a stable formaldehyde gaseous mixture should be produced at temperatures of 150^{o} - 200^{o}C.) It is expected that at a temperature between 150^{o} and 200^{o}C the polymer will decompose to the monomer under steady state conditions to form a constant gaseous mixture with N_2.

Inlet System

Preliminary evaluation of the AUTOSPECT instrumentation system has shown it to be an extremely valuable instrument in measuring exhaust oxygenates, but has demonstrated the need to improve the sample inlet system. It was found for instance that special care must be taken to prevent formaldehyde polymer condensation in the sample lines. With this in mind, a new sample-reagent gas mixing system has been developed as shown in Figures 14-16.

To minimize the length of auto exhaust sample line at atmospheric pressure, the reagent gas mixing chamber and pressure reduction point have been extended out from the main mass spectrometer unit, thereby decreasing the time the sample is present in the inlet system at pressure above 1 mm Hg. This minimizes the number of formaldehyde collisions with the tubing walls; and as an extremely important feature, decreases the effective instrument response time.

The bulk of sampling lines and the fixed leaks has been constructed of glass to enable visual detection and prevention of

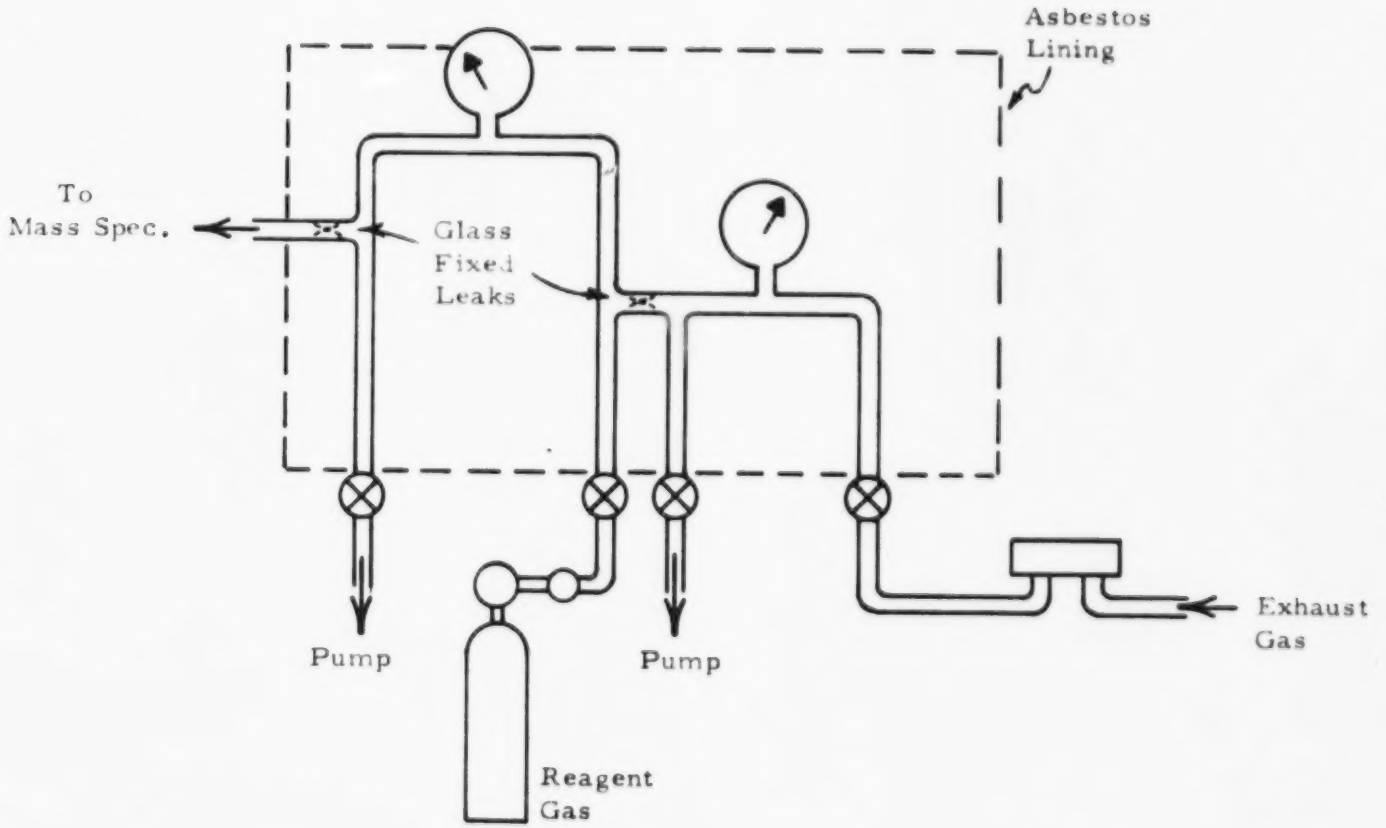

Figure 14 Schematic Diagram of New Inlet System

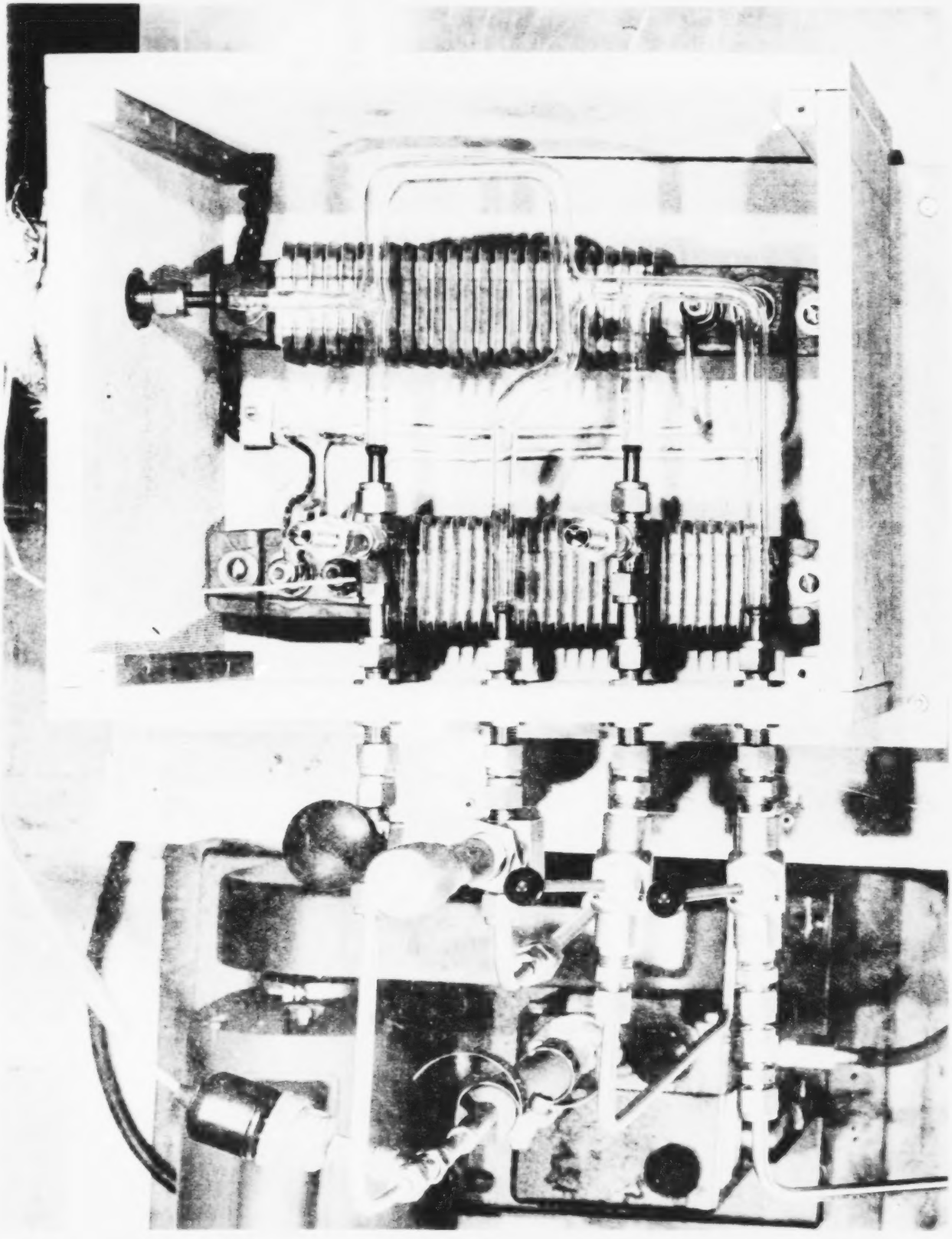

Figure 15. Overview of Reagent - Sample Mixing Oven.

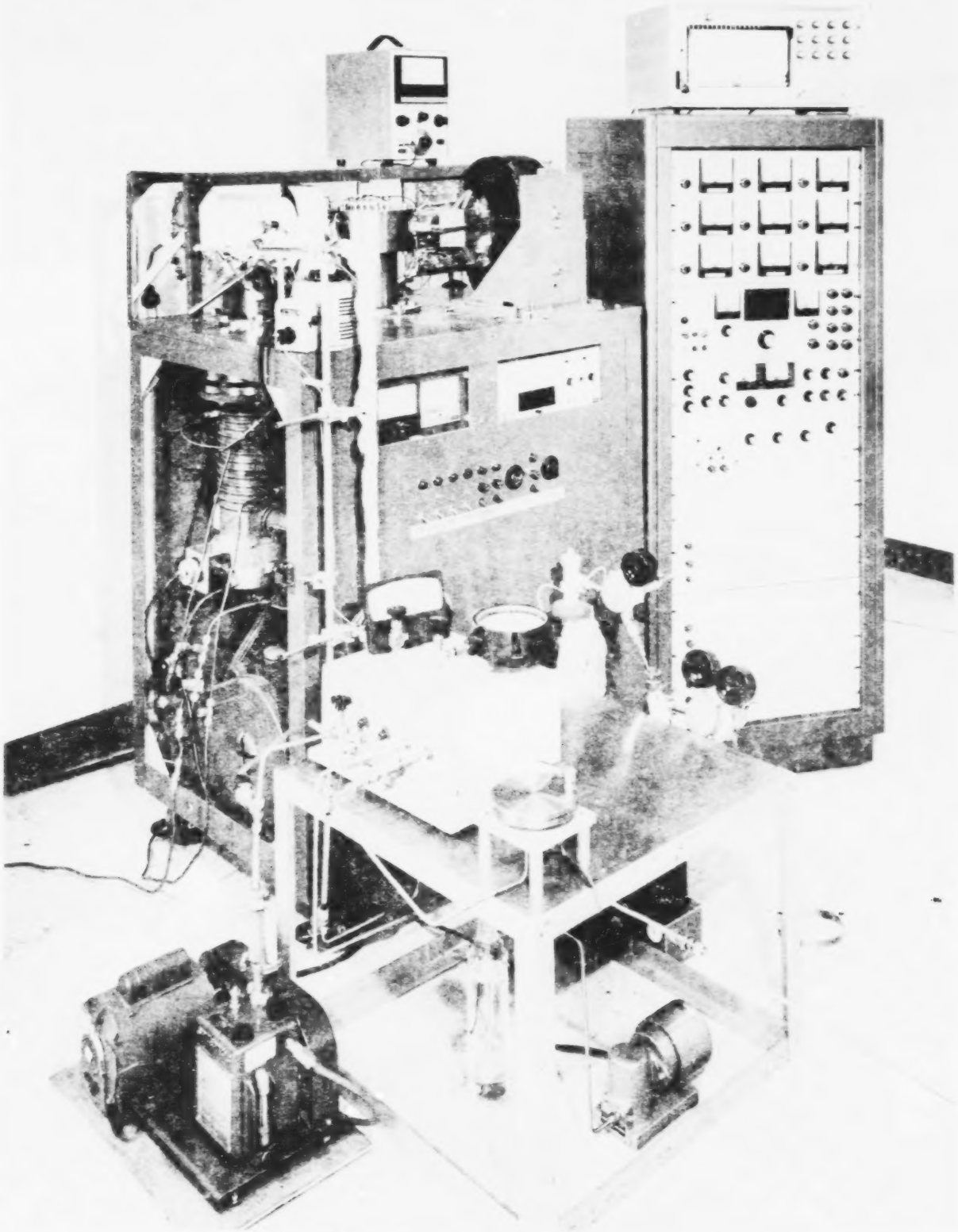

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Figure 16. View of AUTOSPECT with New Inlet System Attached.

any polymer deposition. Distortions in the flow pattern of exhaust sample have been eliminated as much as possible by eliminating obstructions. An example of this is the replacement of stem valves with ball joint valves wherever possible. The Sample-Reagent Mixing Oven was completely redesigned to provide optimum conditions for efficient sample mixing without contamination or sample loss.

The design of the inlet oven as snown in Figure 14 serves a five-fold purpose:

(1) To dynamically mix the automobile exhaust flow with the reagent gas in a fixed proportion. (This proportion may be varied by altering the valve settings.)

(2) To cause a rapid transit of exhaust sample to the mass spectrometer.

(3) To maintain a constant pressure drop from 760 mm Hg down to 1 mm Hg.

(4) To prevent any deposition of contaminant on the walls and

(5) To prevent any electrical discharge from the high voltage mass spectrometer source.

The gas flow system is constructed of glass and maintained at a temperature of 150° - 200°C by two space heaters regulated

by a constant voltage source inside an asbestos concrete oven. These heaters are controlled by a thermistor. The oven is divided into three different pressure ranges by two glass fixed leaks. The first chamber is maintained at near atmosphere pressure and contains a continuous flow of around 2 liters/minute of auto exhaust sample. The second chamber is maintained at a pressure between 200 and 600 mm Hg and contains a continuous flow of a mixture of reagent gas and exhaust sample. Pressure and reagent gas flow rate in this chamber can be independently varied by metering the reagent gas into the chamber and by adjusting a variable conductance valve between the chamber and a mechanical valve. The third chamber is maintained at a pressure of 1 mm Hg by the second fixed leak and is connected directly to the source by a long length of heated glass tubing. A 0-760 Torr pressure gauge is connected to each chamber.

The operation of the middle chamber of this inlet system determines the effective machine response time, the effective sensitivity, and prevents any electrical discharge from the high voltage source. The pressure in this part of the system is continuously maintained at a pressure above 100 mm Hg to prevent

a discharge through the gas to ground. An optimum ratio of reagent gas to sample has been determined experimentally to be such that the available ionizing reagent gas is not saturated during high outputs of sample hydrocarbons and water vapor.

There is six inches of tubing between the fixed leaks to allow for the complete mixing of the reagent gas and exhaust gas. The transit time between these two fixed leaks is the major factor in determining the instrument response time. A small aliquot of the gas mixture passes through the second fixed leak to the mass spectrometer inlet line. This is a 1/4" O.D. heated glass tube which carries the gas mixture at a pressure of 1 Torr from the mixing oven to the mass spectrometer source. This permits the transfer of the sample from the point of sampling to the mass spectrometer itself at a low pressure so that a minimum number of wall collisions occurs and thus a minimum amount of sample is lost.

Ammonia as a Reagent Gas

Ammonia appeared to be a good choice as a reagent gas since it has a proton affinity of 202 Kcal/mole[5]. This proton affinity would enable it to distinguish between the unsaturated aldehydes and their hydrocarbon interferences. The hydrocarbons have proton affinities of 120-180 Kcal/mole[6] while the unsaturated aldehydes are believed to have proton affinities around 200 Kcal./mole. The spectra of pure ammonia at 0.7Torr is shown in Figure 17. The peaks at m/e 17, 18, 35 and 52 are produced by the NH_3^+, NH_4^+, $N_2H_7^+$ and $N_3H_{10}^+$ ions respectively. These ions participate in the following reaction scheme. Ammonia, under electron bombardment, provides NH_3^+ ions which then react with neutral ammonia via ion-molecule reactions:

$$NH_3^+ + NH_3 \longrightarrow NH_4^+ + NH_2$$

$$NH_4^+ + NH_3 \rightleftharpoons N_2H_7^+$$

$$N_2H_7^+ + NH_3 \rightleftharpoons N_3H_{10}^+$$

The resultant equilibria provide steady state concentrations of NH_4^+, $N_2H_7^+$ and $N_3H_{10}^+$ ions which are available to react with any sample molecules present. The reaction mechanism would be expected to proceed via a proton transfer from one of the reagent ions (NH_4^+, $N_2H_7^+$) to the sample molecule.

$$NH_4^+ + A \longrightarrow AH^+ + NH_3$$

The products of these reactions would then be expected to have an m/e value of one greater than the molecular weight of the sample.

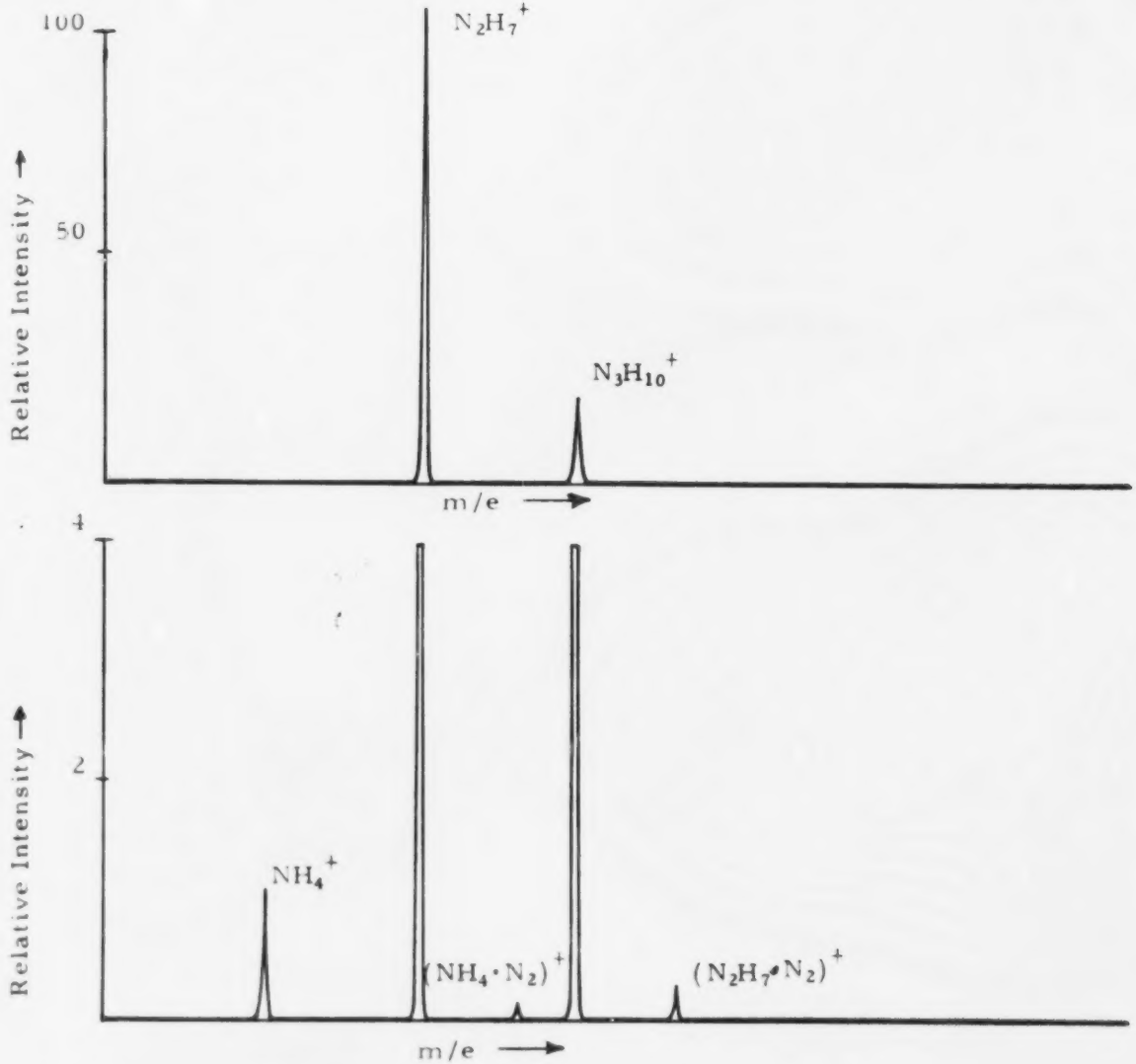


Figure 17 Spectrum of Ammonia at 0.7 Torr, 50°C.

However, it was found that the chemical ionization of aldehydes via an ammonia reagent gas produced ions at the same m/e value as the molecular weight of the sample. This phenomena is demonstrated in Figure 18. Here the chemical ionization of acrolein by ammonia produces a strong peak at m/e 56 and no significant MW + 1 peak at m/e 57. There are two possible mechanisms which may explain the observed results. A direct charge transfer process may occur whereby the sample molecule is ionized by a collisional transfer of an electron from the sample molecule to the reagent ion:

$$NH_4^+ + A \longrightarrow A^+ + NH_4 \downarrow NH_3 + H$$

An alternative process involves the addition of the ammonium ion to the sample molecule with subsequent loss of a water molecule to form the amine ion.

$$\underset{(M/e=18)}{NH_4^+} + \underset{(m/e=M)}{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}H} \longrightarrow \underset{(m/e=M+18)}{(R\text{-}\overset{O}{\overset{\|}{C}}H\cdot NH_4)^+}$$

$$\underset{(m/e=M+18)}{(R\text{-}\overset{O}{\overset{\|}{C}}H\cdot NH_4)^+} \longrightarrow \underset{(m/e=18)}{H_2O} + \underset{(m/e=M)}{(R\text{-}\overset{H}{\overset{|}{C}}=NH_2)^+}$$

This results in a production of an ion with the same molecular weight as the sample molecule; however its structure is somewhat different.

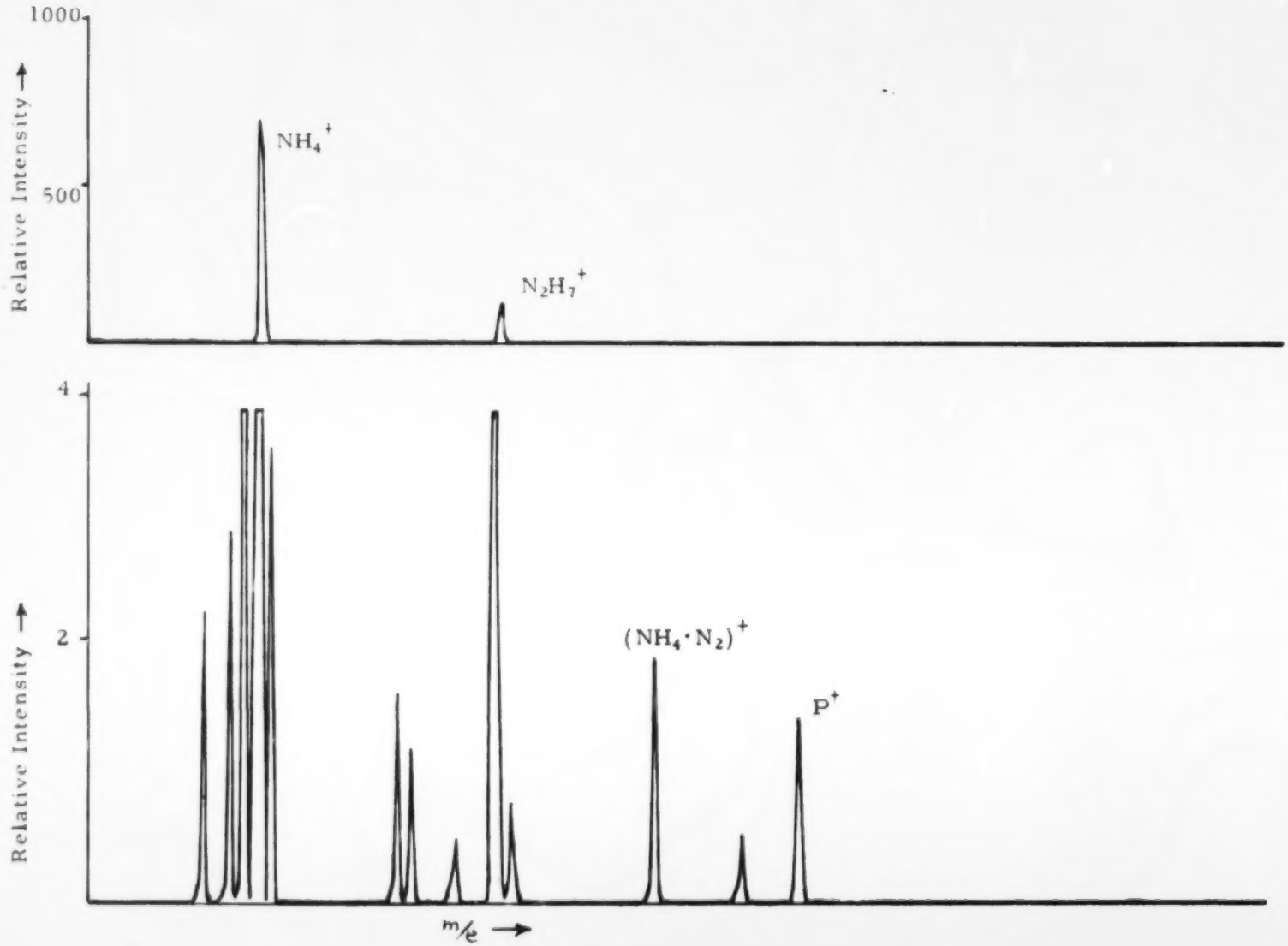


Figure 18 Chemical Ionization Spectrum of Acrolein (Ammonia Reagent)

The latter process appears to be the more probable explanation at the present time. Future experiments should definitely determine the mechanism of the ionization of aldehydes by ammonia under chemical ionization conditions.

These experiments will include an investigation of this ionization process with a deuterated ammonia and an attempt to observe the metastable peaks. These peaks should result from the decomposition of the additive species to form the amine ion. The metastable for the decomposition of acrolein-ammonium ion to the corresponding amine would be

$$m = \frac{m_f^2}{m_i} = 43.32$$

The observance of this metastable ion would demonstrate the reaction pathway and provide proof of this reaction mechanism.

RESULTS AND DISCUSSIONS

Chemical ionization measurements have been made on several different aldehydes and known hydrocarbon interferences, using both methane and ammonia as reagent gases. The mass spectra obtained on one particular series of runs with both reagent gases is shown in Figures 19 thru 27. A summary of relative sensitivities is shown in Table IV.

These series of measurements were carried out using the new heated inlet system and calibrations were made using constant diffusion rates of samples as discussed previously. The diffusion tubes containing the samples were, in the case of acetaldehyde, acrolein, propionaldehyde and pentene, held at room temperature and in the case of crotonaldehyde, benzaldehyde and xylene, held at 80°C in a constant temperature air bath. In the case of butene, a static mixture was made up on a gas vacuum line with methane and ammonia. All the runs were conducted at a source pressure of 0.7 Torr. A source temperature of 200°C and an electron emission current of 200 microamperes were continuously maintained during each experiment.

Table IV: Relative Sensitivities of Important Aldehydes and Hydrocarbons Measured in a Series of Runs Under Chemical Ionization Conditions at 200°C Using Methane and Ammonia as Reagent Gases.

Compound	Molecular Weight	Concentration (ppm)	Sensitivity with CH_4 (10^{-10} amps/ppm) $P+1$	Sensitivity with NH_3 (10^{-10} amps/ppm) P
Acetaldehyde	44	348	0.45	0.003
Acrolein	56	12	0.85	0.050
Propionaldehyde	58	120	2.00	0.600
Crotonaldehyde	70	47	3.80	0.350
Benzaldehyde	106	1	4.00	1.000
Butene	56	74	1.50	0
Pentene	70	83	1.20	0
Xylene	106	7	3.20	0

The results of these sensitivity measurements point out the ability of ammonia to selectively ionize aldehydes and not their hydrocarbon interferences. Note the lack of sensitivity of the alkenes with ammonia. The sensitivities of the homologous group of aldehydes and hydrocarbons show a general increase in sensitivity with an increase in molecular weight. This is to be expected because the increase in size of the molecule increases the ionization cross section and thus the probability of being ionized and detected. One of the reasons for some deficiency of proportionality of molecular weight with sensitivity is due to the fact that the constant temperature air bath was not part of the final engineered version of the calibration system and slight discrepancies in temperatures did exist.

The ability of ammonia to selectively ionize aldehydes has one disadvantage in that it will not ionize formaldehyde to a sufficient degree, and the sensitivity with acetaldehyde is low. However, since formaldehyde and acetaldehyde have no hydrocarbon interferences, methane will still be an ideal reagent gas for

these. Hence, it appears that a dual reagent system is most suitable for the accurate measurement of each of the aldehydes present in raw exhaust gases.

Following are a series of mass spectra which illustrate the advantages and disadvantages of each of the two reagent gases presently under consideration. These spectra were taken by the AUTOSPECT while it was operating in the scanning mode. Since this instrument was designed and built as a direct reading mass spectrometer, its operation in the scanning mode provides mass spectra of somewhat lower quality than would be expected of an instrument designed as a scanning mass spectrometer. Therefore, a chemical ionization quadrupole mass filter was used to determine the total spectra of aldehyde and hydrocarbon samples using methane and ammonia as the reagent gases.

The liquid samples were put in diffusion tubes which were placed in a stream of nitrogen gas. The nitrogen stream was then mixed with the reagent gas and passed over a probe leading to the mass spectrometer source. Gaseous samples were mixed directly with the nitrogen stream.

Since the sensitivity of chemical ionization has already been determined, these experiments were carried out mainly to define the relative sensitivity of the instrument to each sample with different reagent gases.

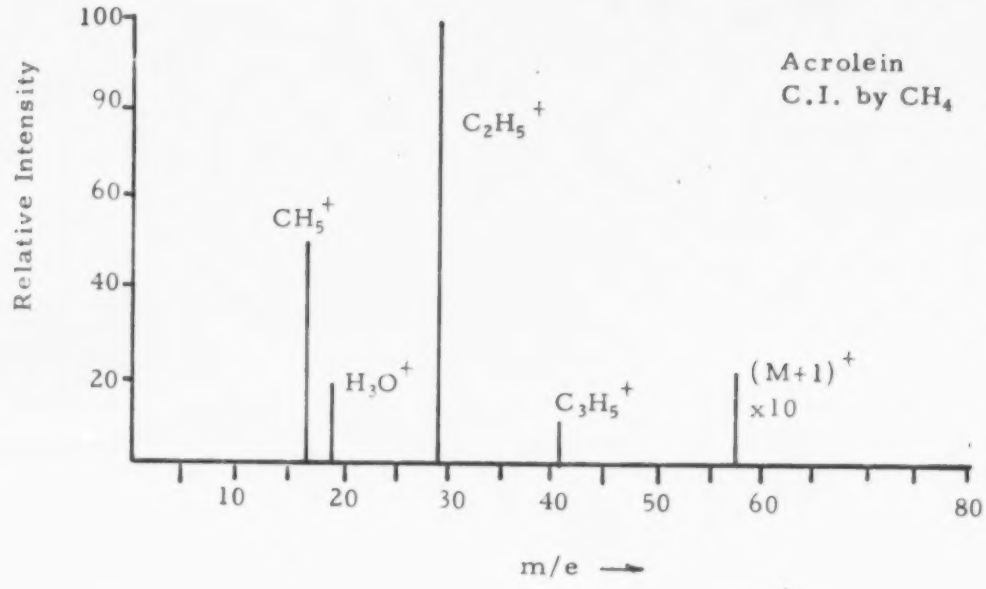
The concentration of each aldehyde and hydrocarbon is the same for both reagent spectra. The concentration of each aldehyde and its respective interfering hydrocarbon is approximately similar. The lower molecular weight samples are less than 100 ppm while the higher molecular weight samples are around 1 ppm.

The presence of the reagent ions (CH_5^+, $C_2H_5^+$, $C_3H_5^+$ for methane and NH_4^+, $N_2H_7^+$ for ammonia) does not interfere with the measurement of any of the aldehydes. However, methane does ionize water via proton transfer (to m/e 19) and also causes some fragmentation of the alkenes (to m/e 43). Ammonia does neither of the above and as a result produces less extraneous ions in the spectra even though it does apparently react with nitrogen to form an agglomerate ion (m/e 46).

The utility of ammonia as a reagent gas is demonstrated quite effectively by comparing Figure 19 with Figure 20. Both acrolein and butene produce an M+1 peak when ionized by methane. Thus the presence of butene in a sample would extensively interfere with the measurement of the proper concentrations of acrolein.

However, a comparison of the two plots in Figure 20 shows that while ammonia will produce a substantial M^+ peak for acrolein (m/e = 56) it will produce virtually no M^+ peak for butene. Thus the measurement of the M^+ peak of acrolein in ammonia will not be affected by the presence of butene in the sample.

The same phenomena is true for crotonaldehyde. The chemical ionization of crotonaldehyde by methane (Figure 21) produces ions at m/e 71 (M+1) but ions at this mass may also be produced by the chemical ionization of pentene by methane. Ammonia, however, serves as a good reagent gas for crotonaldehyde (Figure 22) producing the M^+ ions at m/e 70, while producing no significant ionization of pentene in the interfering mass range.



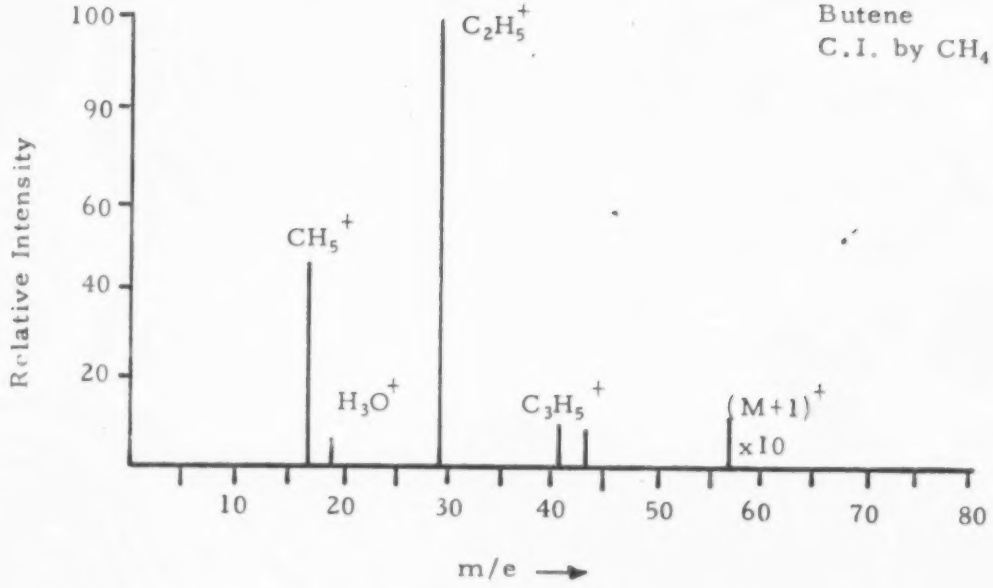
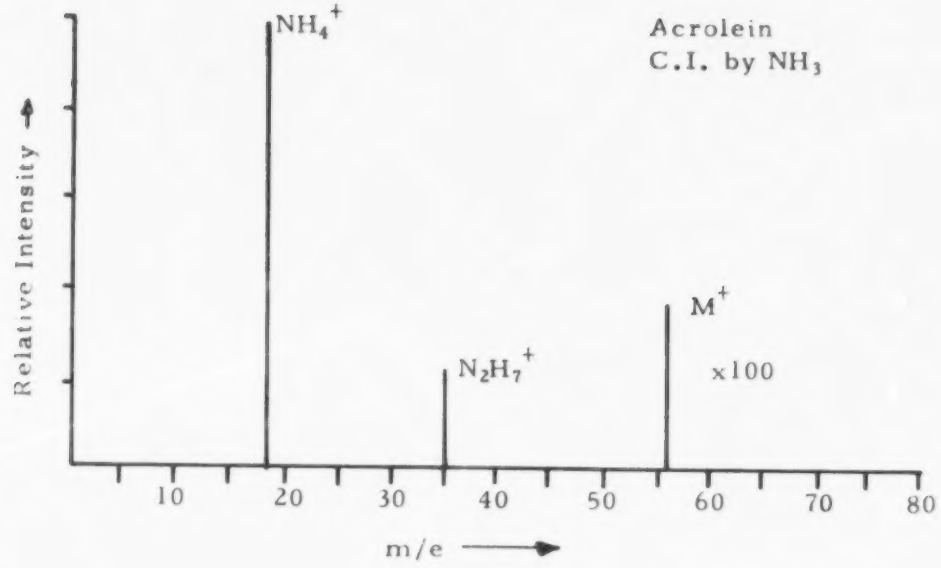


Figure 19 Spectra of Acrolein and Butene via C.I. by Methane



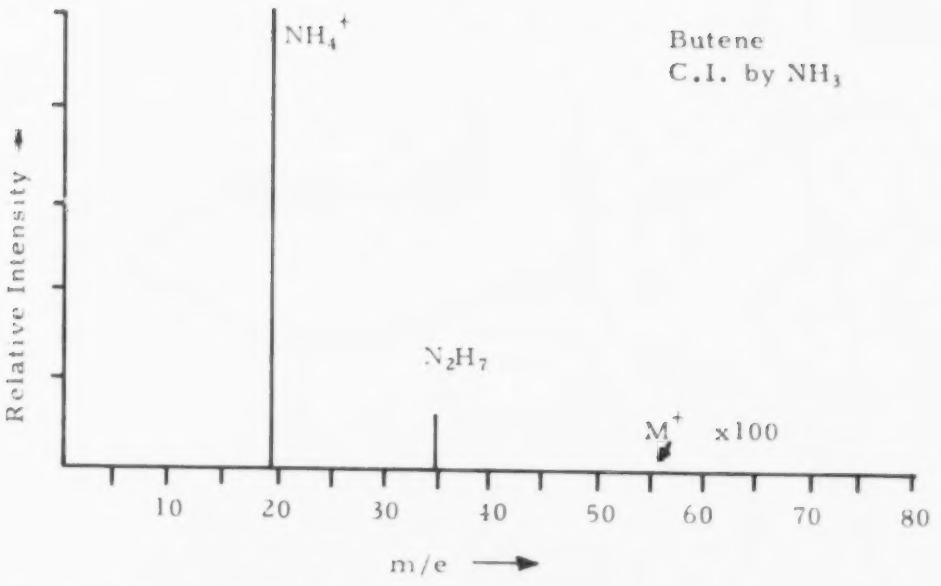
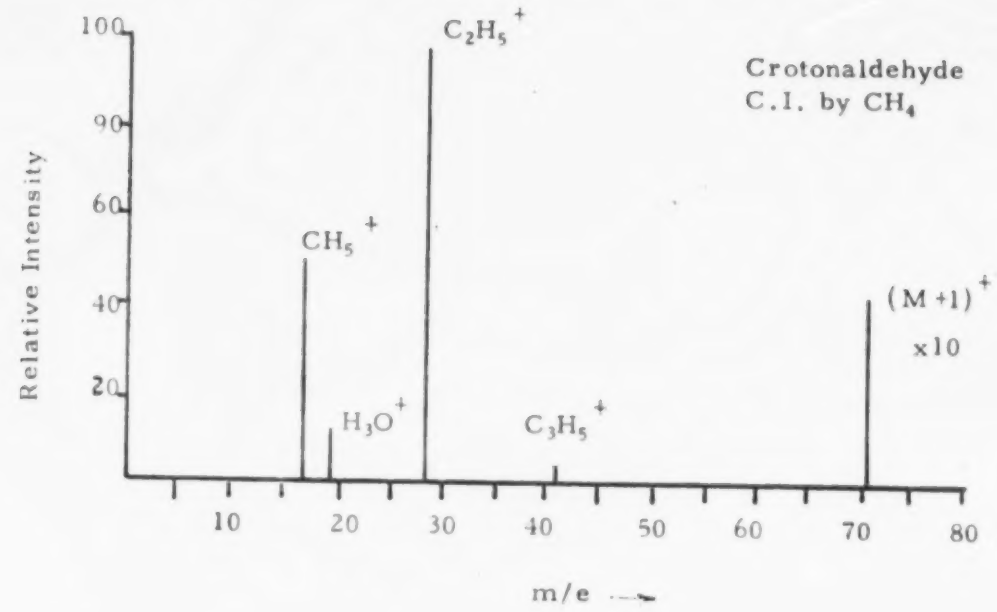


Figure 20 Spectra of Acrolein and Butene via C.I. by Ammonia



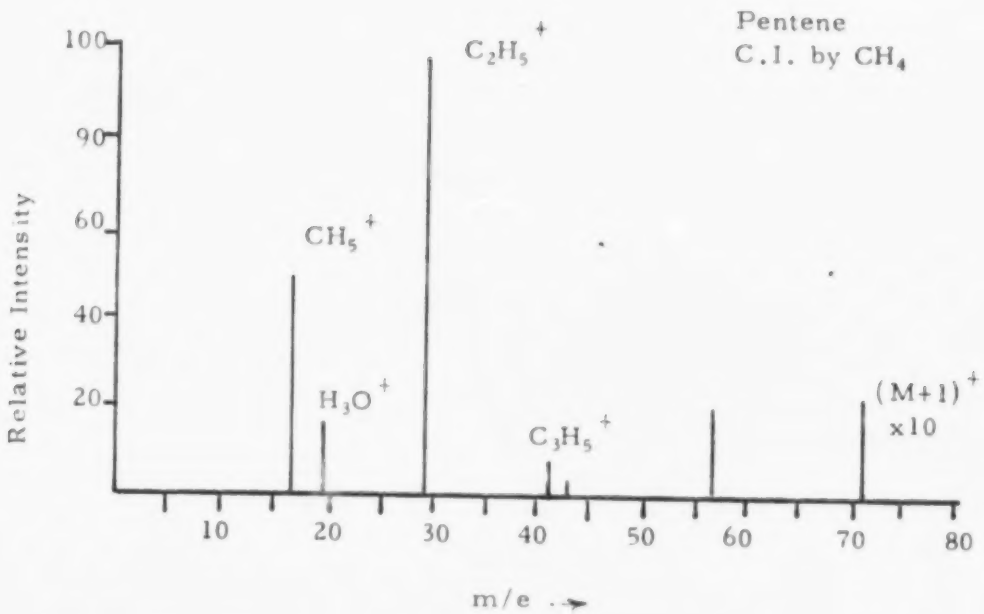
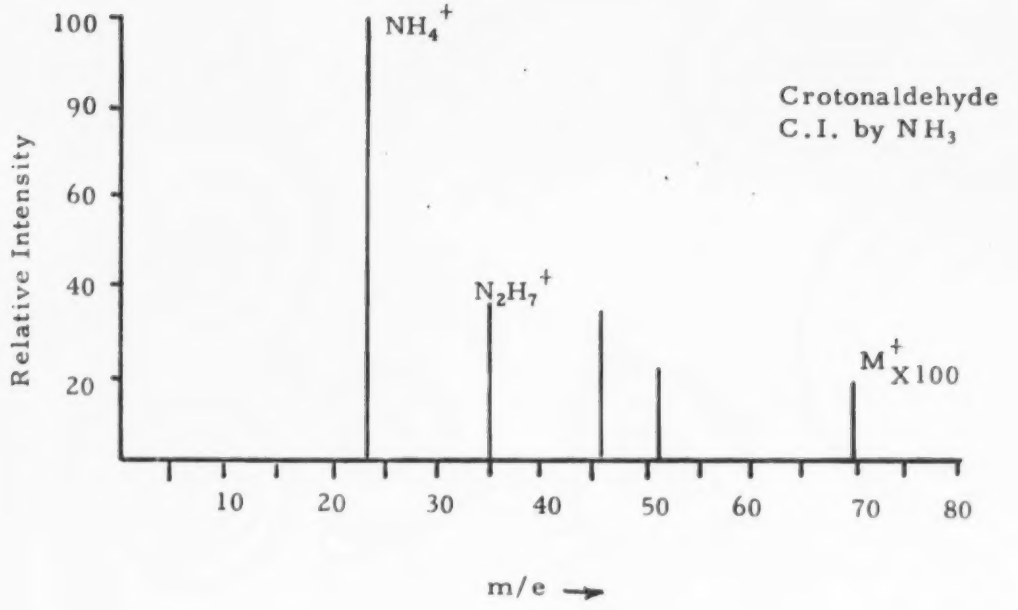


Figure 21 Spectra of Pentene and Crotonaldehyde via C.I. by Methane



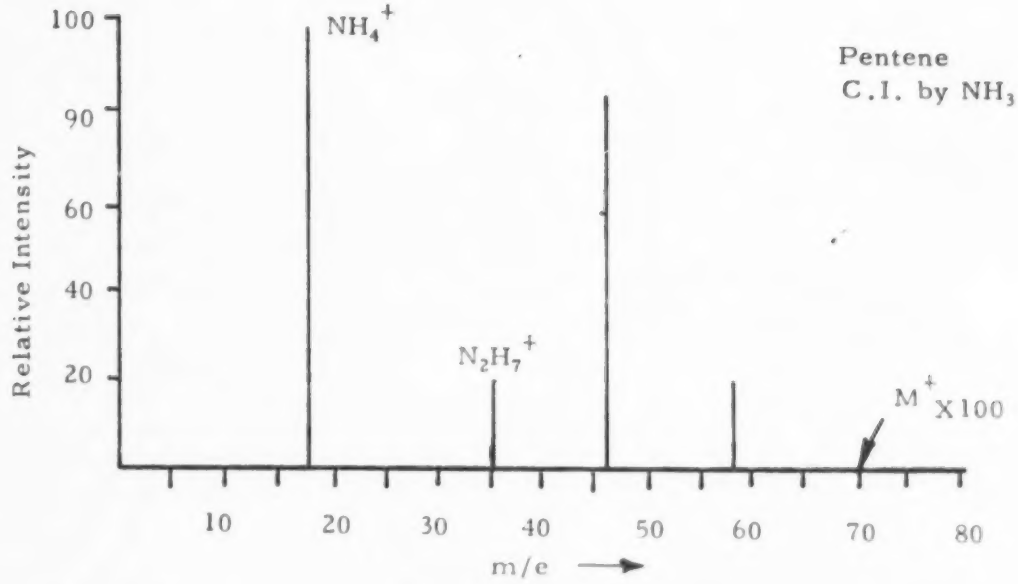


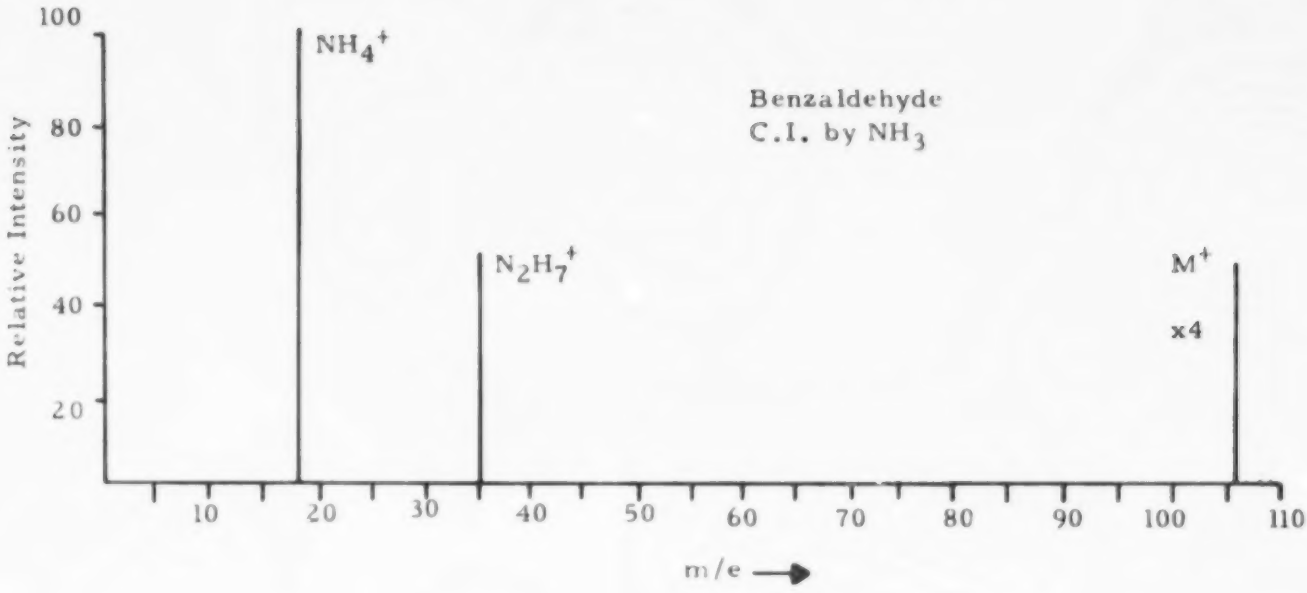
Figure 22 Spectra of Pentene and Crotonaldehyde via C.I. by Ammonia

The effectiveness of ammonia is again demonstrated (Figure 23) by its ability to specifically ionize benzaldehyde in the presence of xylene. While methane will ionize both samples to produce interference (Figure 24).

Several of the aldehydes studied with methane chemical ionization did not show interferences from any alkenes. These aldehydes were also studied using ammonia as the reagent gas. As can be seen in Figures 25-27 the sensitivity of the ammonia reagent gas increases as the molecular weight of the aldehyde increases.

The sensitivity for formaldehyde is small, while it is moderate for acetaldehyde and acceptable for propionaldehyde. Methane is a suitable reagent for these oxygenates since it provides good sensitivity with no interferences.

These results indicate that the best method , at present, for the analysis of aldehydes in auto exhaust is the use of two reagents in the chemical ionization process. Methane provides the maximum sensitivity for formaldehyde, acetaldehyde, and propionaldehyde, butyraldehyde, and v-leraldehyde while ammonia



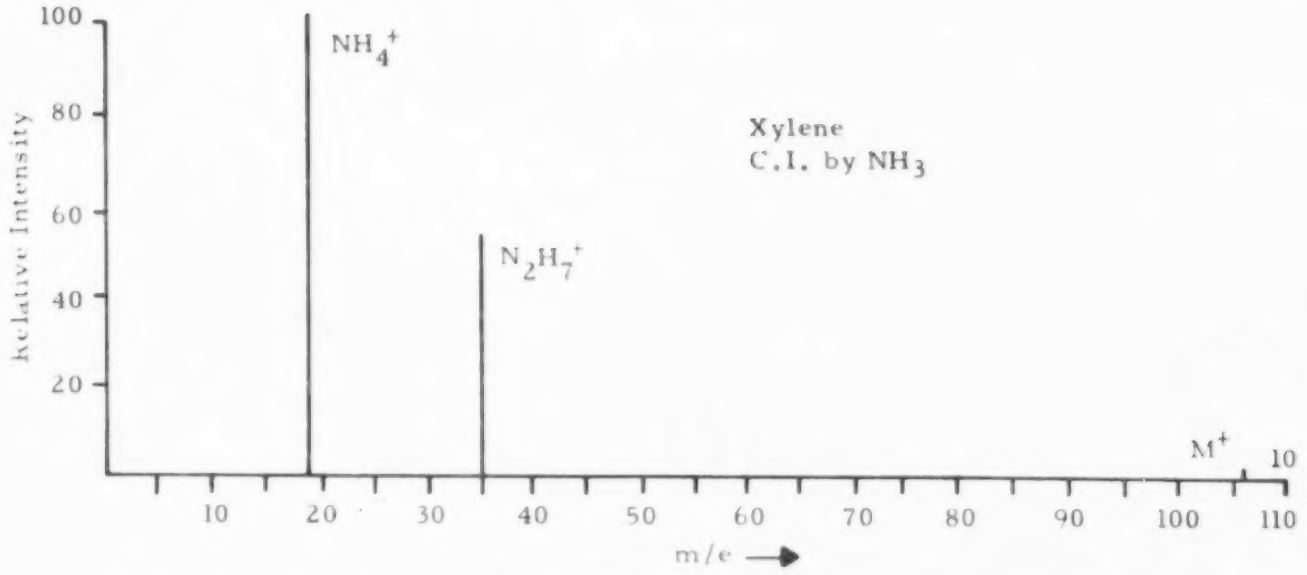
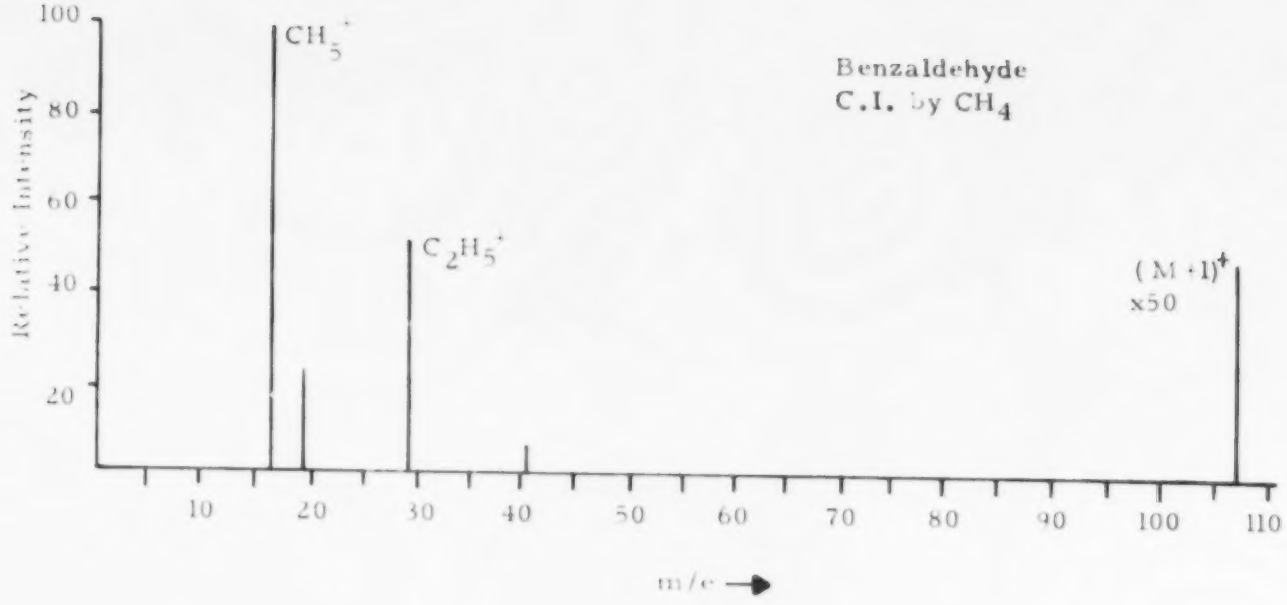


Figure 23. Spectra of Xylene and Benzaldehyde via C.I. by Ammonia



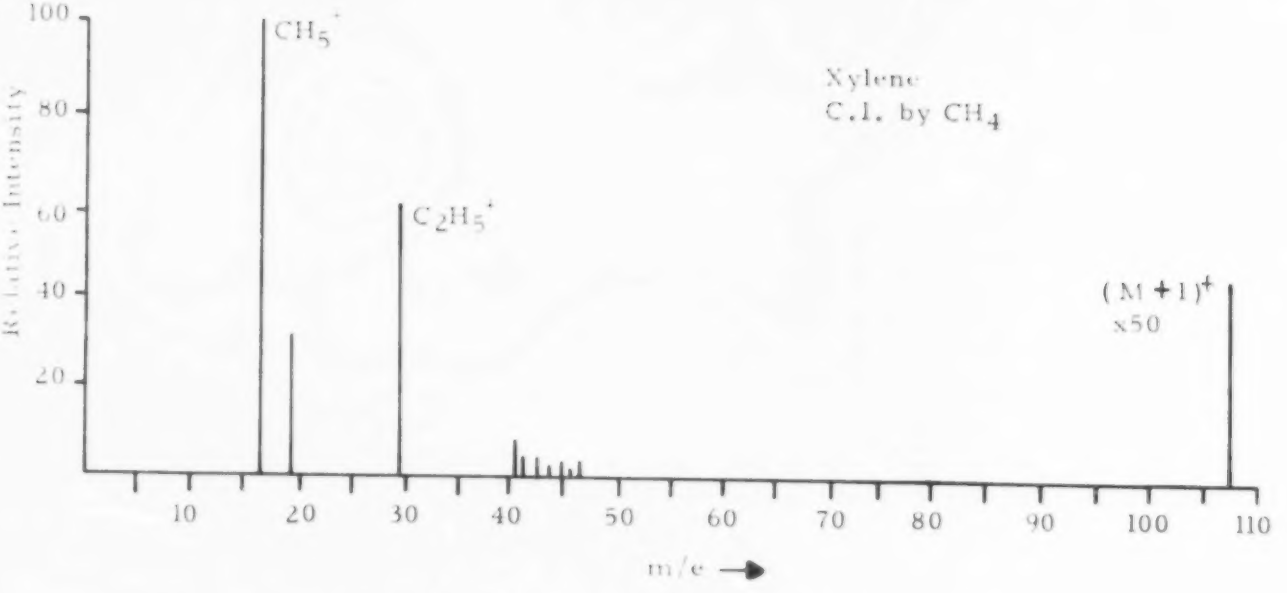
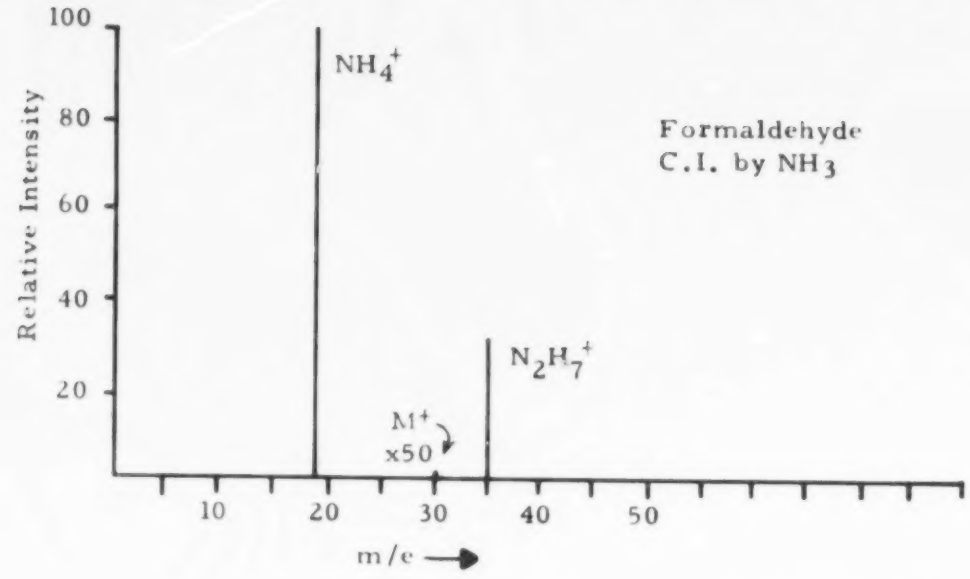


Figure 24. Spectra of Xylene and Benzaldehyde via C.I. by Methane



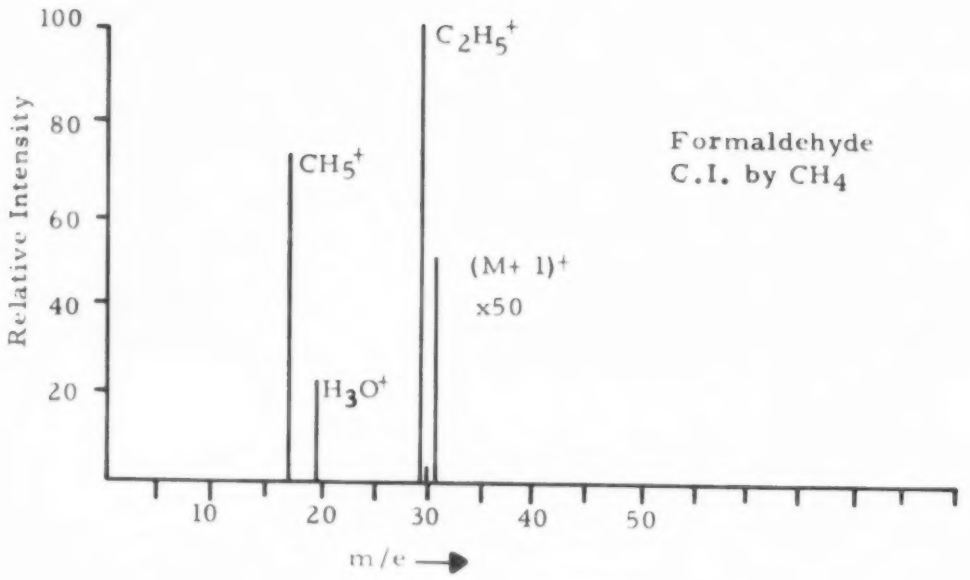
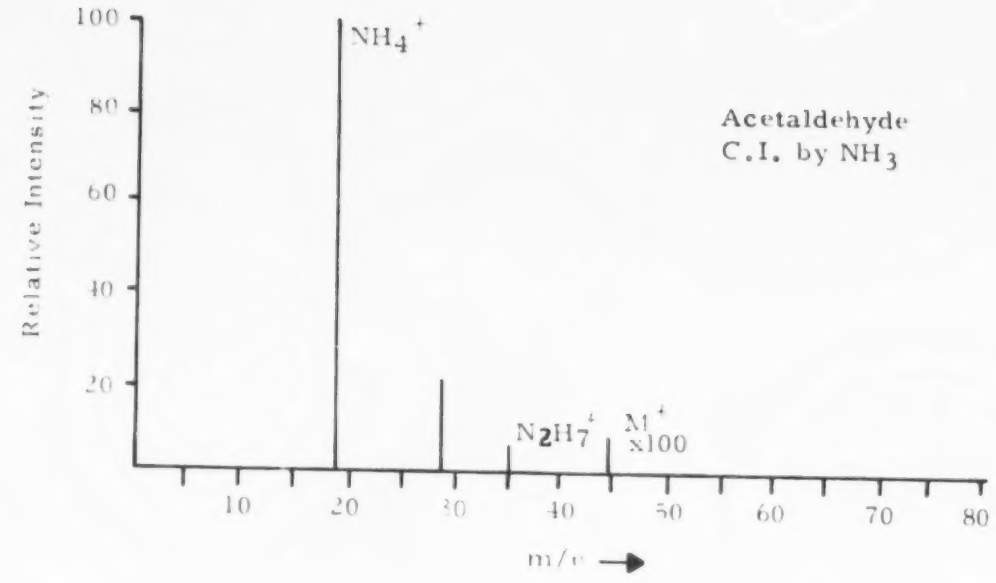


Figure 25. Spectra of Formaldehyde via C.I. by Methane and Ammonia.



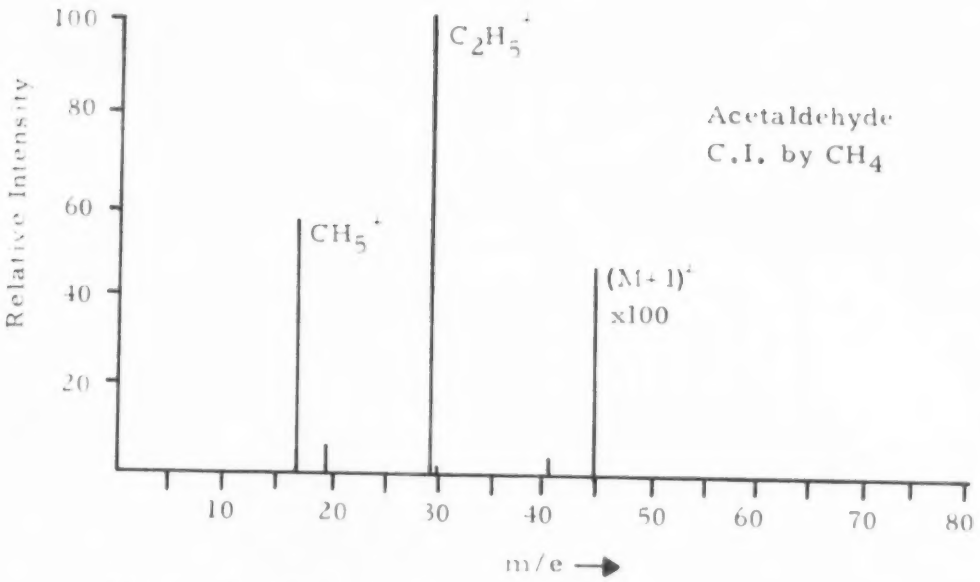
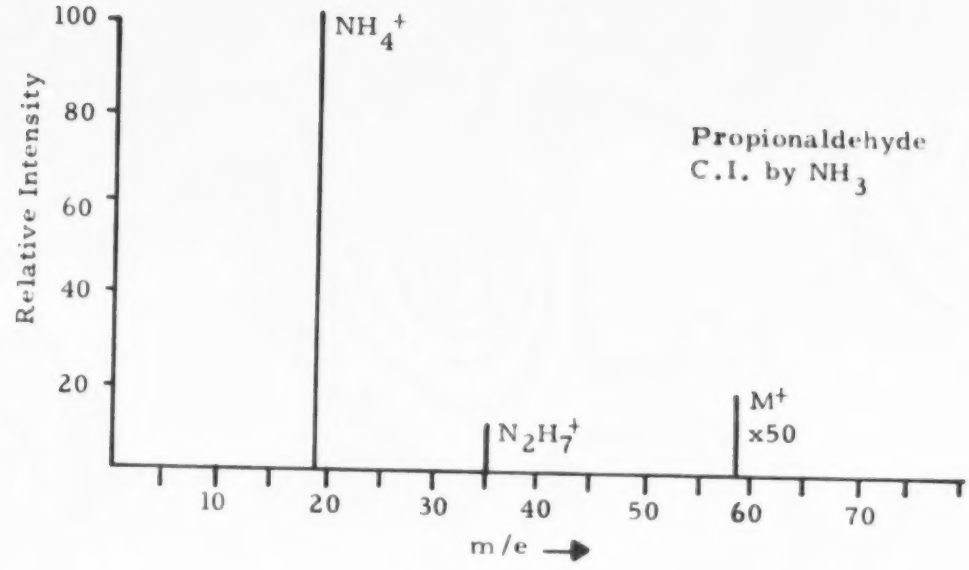


Figure 26. Spectra of Acetaldehyde via C.I. by Methane and Ammonia.



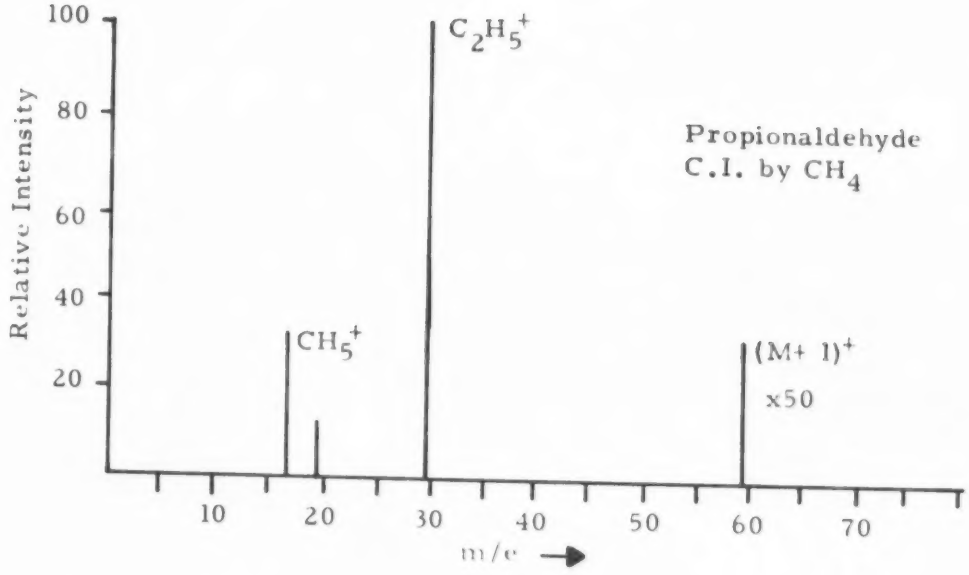


Figure 27. Spectra of Propionaldehyde via C.I. by Methane and Ammonia.

provides good sensitivity for acrolein, crotonaldehyde, benzaldehyde and tolualdehyde with freedom from interference.

The improvements in the calibration and inlet systems have increased the response time as well as the sensitivity. These advancements have also increased the accuracy of the total instrument. Further improvements and the completion of detailed experiments will culminate in a successful establishment of the ultimate sensitivity of this method.

APPENDIX

Example Calculation of Diffusion Constant for Benzaldehyde

Method of Fuller Schettler and Giddings

$$D = \frac{10^{-3}\, T^{1.75} \left(\frac{1}{M_A} + \frac{1}{M_b}\right)^{\frac{1}{2}}}{P\left[(\Sigma_A \nu_i)^{\frac{1}{3}} + (\Sigma_B \nu_i)^{\frac{1}{3}} \right]^2}$$

$$D = \frac{10^{-3}\, (273)^{1.75} \left(0.0371 + 0.0094\right)^{\frac{1}{2}}}{1\left[(17.9)^{\frac{1}{3}} + (62.9)^{\frac{1}{3}} \right]^2}$$

$$\frac{18.3\, (0.0451)^{\frac{1}{2}}}{(7.45)^2}$$

$$D = 0.0702 \frac{cm^2}{sec}$$

$M_A = 28\ (N_2)$

$M_B = 106$ Benzaldehyde

$\Sigma_A \nu_i = 112.66$

P= 1 atm

T = 273 dg. Kelvin

Method of Roberts

$$D = 4.44 \left[\left(\frac{E}{K}\right)^{-0.5} \quad d^{-1.5} \quad \left(1. - 0.5\sigma^{0.6}\right)^{-1}_{-1} \right]^{0.75}$$

where $\frac{E}{K} = \frac{0.75 T_b}{0.574 + \Sigma \Delta T}$ $\qquad d = \left(\frac{E\, Ve}{1.265}\right)^{\frac{1}{3}}$ $\qquad \sigma = \frac{\mu^2}{2\, E d^3}$

$T_b = 452^0 K$

$\Sigma \Delta T = 0.094$

Ve= 319.1 cm/gm. mole

μ = 2.00 ESU centimeters

Method of Roberts

$$\frac{E}{K} = \frac{(0.75)\ (452)}{(0.574+0.094)}$$

$$d^3 = \frac{(7.01 \times 10^{-2})\ 455}{(1.265)}$$

$$\sigma = \frac{(2.00)^2}{2(7.01 \times 10^{-2})\ (2.52)}$$

$E = 7.01 \times 10^{-2}$ $\quad d^3 = 2.52 \times 10^{2}$ $\quad \sigma = .113$

$$D = 4.44 \left[(7.01 \times 10^{-2})^{-0.5} (2.52 \times 10^{2})^{-0.5} \left[1-(0.5)(0.113)^{0.6} \right]^{-1} \right]^{0.75}$$

$D = 0.0599$

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